CHAPTER 1
INTRODUCTION TO NANOMATERIALS AND FUEL CELLS

1.1 OUTLINE OF NANOTECHNOLOGY

Nanotechnology involves the creation and/or manipulation of materials at nanometer scale either by scaling up from a single group of atoms or by refining or reducing bulk materials. A nanometer is $1 \times 10^{-9}$ m or one millionth of a millimeter (mm). Generally, nanotechnology deals with structures, sizes from 1 to 100 nanometers in at-least one-dimension and involves developing materials or devices possessing within that size. All materials are composed of grains, which in turn comprise many atoms. These grains are usually invisible to our naked eye depending on their size. Conventional materials have grains varying in size anywhere from several microns ($\mu$m) to millimeters (mm). The average size of an atom is on the order of 1 to 2 angstroms (Å) in radius. One nanometer comprises $10$ Å, and hence in 1 nm, there may be 3-5 atoms, depending on the atomic radii. Nanocrystalline materials are exceptionally strong, hard and ductile at high temperatures, wear-resistant, erosion-resistant, corrosion-resistant and chemically active. Since nanoparticles contain a proportionately large number of surface atoms, there are a significantly greater number of adsorption/reaction sites that are available to interact with the surrounding environment. Further, whereas bending of a bulk metal occurs via movement of grains in the $>100$ nm size regime, metallic nanostructures will have an extreme hardness with significantly different malleability/ductility relative to the bulk material.
Quantum mechanical effects are important at the nanoscale, which is in the quantum realm. Nanotechnology is diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly. Nanotechnology can create numerous materials and devices with a vast range of applications such as in medicine, electronics, biomaterials and energy production. Nanotechnology is the engineering of functional systems at the molecular scale. In its original sense, nanotechnology refers to the projected ability to construct items from the bottom-up / top-down, using techniques and tools being developed today (Charles et al., 2003).

Nanoparticles were used by Artisans as far back as the 9th century in Mesopotamia for generating a glittering effect on the surface of the pots. Even these days, potteries from the middle ages and Renaissance often retain a distinct gold or copper coloured metallic glitter. This so called cluster is caused by a metallic film that was applied to the transparent surface of a glazing. The cluster originated within the film itself, which contained silver and copper nanoparticles dispersed homogeneously in the glassy matrix of the ceramic glaze. These nanoparticles were created by the Artisans by adding copper and silver salts and oxides together with vinegar, ochre and clay on the surface of previously-glazed pottery. The object was then placed into a kiln and heated to about 600 °C in a reducing atmosphere. In the heat the glaze would soften, causing the copper and silver ions to migrate into the outer layers of the glaze. There is a reducing atmosphere reduced the ions back to metals, which then came together forming the nanoparticles that give the color and optical effects.
Fig. 1.1 Ancient stained-glass coated with gold and silver nanoparticles.
1.1.1 Richard Feynman hypothesis

The amount of space available to us for information storage (or other uses) is enormous. As first described in a lecture titled, 'There's Plenty of Room at the Bottom' in 1959 by Richard P. Feynman, there is nothing besides our clumsy size that keeps us from using this space. In his time, it was not possible to manipulate single atoms or molecules because they were far too small for devices. Thus, his speech was completely theoretical and seemingly fantastic. He described how the laws of physics do not limit our ability to manipulate single atoms and molecules due to the lack of methods for nanoscale manipulation. However, he correctly predicted that the time would come for the manipulation of atomically precise matter. Prof. Feynman described such atomic scale fabrication as a bottom up approach, and the top-down approach.

The top-down method involves the construction of parts through methods such as cutting, carving and molding. Using these methods, it is possible to fabricate a remarkable variety of machinery and electronics devices. However, the sizes at which one can make these devices are severely limited ability to cut, carve and mold. Bottom-up manufacturing, on the other hand, would provide components made of single molecules which are held together by covalent forces that are far stronger than the forces that hold them together macro-scale components. Furthermore, the amount of information that could be stored in devices build from the bottom up would be enormous.
**Fig.1.2** Comparison of the surface area/volume ratio of macroscopic ZrO$_2$ balls and nanoscopic ZrO$_2$ particles (Dept. of Materials Engg., University of Concepcion, Chile).

**Fig.1.3** Bottom-up and Top-down fabrication.
“Top-down” – building something by starting with a larger component and carving away material. In nanotechnology: patterning (using photolithography) and etching away material, as in building integrated circuits.

“Bottom-up” – building something by assembling smaller components. In nanotechnology: self-assembly of atoms and molecules, as in chemical and biological systems.

1.1.2 Larger to smaller: a materials perspective

A number of physical phenomena become pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the “quantum size effect” where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro to micro dimensions. However, quantum effects become dominant when the nanometer size range is reached, typically at distances of 100 nm or less. Additionally, a number of physical (mechanical, electrical, optical, etc.) properties change when compared to macroscopic systems. An example is the increase in surface area to volume ratio altering mechanical, thermal and catalytic properties of materials.

Materials reduced to the nanoscale can show different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); stable materials turn combustible (aluminum); insoluble materials become soluble (gold).
A material such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these quantum and surface phenomena that matter exhibits at the nanoscale.

1.1.3 Simple to complex: a molecular perspective

Modern synthetic chemistry has reached the point where it is possible to prepare small molecules to almost any structure. These methods are used today to manufacture a wide variety of useful chemicals such as pharmaceuticals or commercial polymers. This ability raises the question of extending such kind of control to the next-larger level, seeking methods to assemble these single molecules into supramolecular assemblies consisting of many molecules arranged in a well defined manner. These approaches utilize the concepts of molecular self-assembly and/or supramolecular chemistry to automatically arrange themselves into some useful confirmation through a bottom-up approach. The concept of molecular recognition is especially important: molecules can be designed so that a specific configuration or arrangement is favored due to non-covalent intermolecular forces. The Watson–Crick base-pairing rules are the direct result of this, as is the specificity of an enzyme being targeted to a single substrate, or the specific folding of the protein itself. Thus, two or more components can be designed to be complementary and mutually attractive so that they make a more complex and useful whole. Such bottom-up approaches should be capable of producing devices in parallel and be much cheaper than top-down methods, but could potentially be
overwhelmed as the size and complexity of the desired assembly increases. Most useful structures require complex and thermodynamically unlikely arrangements of atoms. Nevertheless, there are many examples of self-assembly based on molecular recognition in biology, most notably Watson–Crick base-pairing and enzyme-substrate interactions. The challenge for nanotechnology is whether these principles can be used to engineer new constructs in addition to the natural one (Watson et al., 1953).

1.1.4 Advancement in nanomaterials

The history of nanomaterials began immediately after the big bang theory, when nanostructures were formed in the early meteorites. Nature later evolved several other nanostructures like seashells, skeletons, etc. Nanoscaled smoke particles were formed during the use of fire by early humans. The scientific story of nanomaterials however, began much later. One of the first scientific report is the colloidal gold particles synthesized by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940’s, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements. Nanosized amorphous silica particles have found large-scale applications in many everyday consumer products, ranging from non-dairy coffee creamer to automobile tires, optical fibers and catalyst supports. In the 1960s and 1970’s metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert-gas
evaporation technique was published by Granqvist and Buhrman (Granqvist et al., 1976). Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its color and its resistance to acids and bio-corrosion are still not understood, but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a superlattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the superlattice are present, as has been shown by the fabrication of synthetic samples.

1.2 PROPERTIES OF NANOMATERIALS

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials. Due to their small dimensions, nanomaterials have an extremely large surface to volume ratio which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable in length, the entire material will be affected by the surface properties of
nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have the spatial confinement effect on the materials, which bring the quantum effects. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelectronics. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are important factors in the determination of the properties of the nanomaterials. Nanosturctures and nanomaterials favors self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced the mechanical properties of nanomaterials will be better than the bulk.

1.2.1 Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry, biomedicine, etc..
Fig. 1.4 Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles (Susie Eustis et al., 2006).
There are several mechanisms for modifying the optical properties of materials and therefore its application in photonic devices. In the nanoparticles with some of its dimensions smaller than 10 nm, new effects came into existence, since the laws of classical physics no longer valid and one needs quantum physics to explain their behavior. For example, the minimum potential energy of an electron confined in a nanoparticle is higher than expected in classical physics and energy levels of different electronic states are discrete. Due to quantum confinement, the particle size has a drastic effect on the density of electronic states and thus on the optical response.

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables, including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have a dramatic influence on optical properties of metal nanostructures. Fig. 1.4 exemplifies the difference in the optical properties of metal and semiconductor nanoparticles. With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed in the different samples of gold nanospheres. However, when an anisotropy is added to the nanoparticle, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.
1.2.2 Electrical properties

The quantum dots and wire or rod like shape of one-dimensional nanostructures has caused them to be the source of somewhat intensifying research of the past several years. In particular, their novel electrical and mechanical properties are the subject of intense research. The category of quantum dots and one-dimensional nanostructures consists of a wide variety of morphologies. Especially, electron transport through ultrasmall structures such as quantum dots is governed by charge and energy quantization effects. Charge quantization comes into play for structures with an extremely small capacitance. The capacitance of a nanostructure, which, roughly speaking, is proportional to its typical linear dimension may become so small that the energy required to charge the structure with one additional charge carrier (electron, hole, cooper pair) exceeds the thermal energy available.

In this case, charge transport through the structure is blocked – an effect which has appropriately been termed the “Coulomb blockade” (CB) effect. This effect can be exploited to manipulate single electrons within nanostructures. Also, because of the smallness of the structures, energy quantization may become considerable. In contrast to bulk structures, charge carriers within a quantum dot are only allowed to occupy discrete energy levels, as in the case of electrons within an atom. In a manner resembling scattering effects known from atomic and nuclear physics, the occurrence of these discrete energy levels can modify the charge transport characteristics of
ultrasmall devices. In metallic nanostructures, Coulomb blockade can also occur without “quantum aspects”, as the energy level spacing in these structures is usually too small to be observable. In fact, energy quantization is the reason for the name “quantum dot” and differentiates this from most of the metallic nanostructures. However, in extremely small metallic nanoparticles and clusters, quantum effects can also be considerable.

The peculiar properties of quantum dots described above may be used in a variety of device applications. The most important of these features are the discrete energy spectrum, the smallness of the capacitance, and (which is related) the possibility of manipulating single charges. The survey of device applications given in the following sections is by no means complete. It is intended to demonstrate the wealth of work done in the field and the many directions pursued. The possibility of manipulating single charges in single-electron tunneling devices led to early proposals for meteorological applications of the Coulomb blockade effect. Devices called “electron turnstiles” can be used to count single electrons and could form the basis of accurate current standards based on the definition of the second. Also, the electrical behavior of nanostructure materials plays vital role in many applications in recent technologies.
Fig.1.5 Electrical behavior of nanotubes (Collins et al., 2000).
1.2.3 Mechanical properties

Due to the nanometer size, many of the mechanical properties of the nanomaterials are modified to be different from the bulk materials, including the hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength, etc. An enhancement of mechanical properties of nanomaterials can result due to this modification, which are generally resultant from the structural perfection of the materials. The small size, either renders them free of internal structural imperfections such as dislocations, micro twins, and impurity precipitates or the few defects or impurities present cannot multiply sufficient to cause mechanical failure.

1.2.4 Magnetic properties

The magnetic properties of nanosize particles differ from those of bulk mainly in two points. The large surface to volume ratio results in a different local environment for the surface atoms in their magnetic coupling/interaction with neighboring atoms, leading to the mixed volume and surface magnetic characteristics. Unlike bulk ferromagnetic materials, which usually form multiple magnetic domains, several small ferromagnetic particles could consist of only a single magnetic domain. In the case of single particle being a single domain, the super-paramagnetism occurs, in which the magnetization of particles is randomly distributed and they are aligned only under an applied magnetic field and the alignment disappears once the external field is withdrawn.
Fig. 1.6 Magnetic properties of nanostructured materials.
One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects. However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior.

Surface and the core of Au nanoparticles with 2 nm in diameter show ferromagnetic and paramagnetic character, respectively. The large spin-orbit coupling of these noble metals can yield to a large anisotropic and therefore exhibit high ordering temperatures. More surprisingly, permanent magnetism was observed up to room temperature for thiol-capped Au nanoparticles. For nanoparticles with sizes below 2 nm, the localized carriers are in the 5d band. Bulk Au has an extremely low density of states and becomes diamagnetic, as is also the case for bare Au nanoparticles. This observation suggested that modification of the d-band structure by chemical bonding can induce ferromagnetic like character in metallic clusters.

1.2.5 Thermal properties

Many properties of the nanoscale materials have been well studied, including the optical, electrical, magnetic and mechanical properties. However, the thermal properties of nanomaterials have only seen slower progresses. This is partially due to the difficulties of experimentally measuring and controlling the thermal transport in nanoscale dimensions. Atomic Force
Microscope (AFM), and scanning probe microscope (SPM) has been introduced to measure the thermal transport of nanostructures with nanometer-scale, high spatial resolution, providing a promising way to probe the thermal properties within the nanostructures.

1.2.6 Catalytic properties

A larger percentage of surface atoms greatly increase surface activities. The unique surface structure, electronic states and largely an exposed surface area are required for stimulating and promoting chemical reactions. The size dependent, catalytic properties of the nanomaterials have been widely studied while investigations on the shape dependent catalytic behavior are cumbersome.

1.3 CLASSIFICATION OF NANOMATERIALS

Nanostructured materials (NSMs), nanocrystals or nanophase materials are polycrystals with an ultra-fine grain size in the range of 3 to 100 nm. A number of physical and mechanical properties of NSMs have been found to be superior to the properties of conventional coarse-grained polycrystals and are attractive for engineering applications. The nanometers are classified based on their chemical compositions and dimensions as listed in the next page. According to the dimensions, nanomaterials can be divided into zero dimensional, one dimensional, two dimensional and three dimensional nano materials.
3D CONFINEMENT (or) 0-DIMENSIONAL NANOMATERIALS

- Fullerenes
- Colloidal Particles
- Nanoporous Silicon
- Activated Carbons
- Quasi – Crystals
- Semiconductor Quantum Dots
- Semiconductor Particles in a Glass Matrix

2D CONFINEMENT (or) 1-DIMENSIONAL NANOMATERIALS

- Carbon Nanotubes and Filaments
- Metal and Magnetic Nanowires
- Oxide and Carbide Nanorods
- Semiconductor Quantum Wires

1D CONFINEMENT (or) 2-DIMENSIONAL NANOMATERIALS

- Nanolaminated or Compositionally modulated Materials
- Grain Boundary Films
- Clay Platelets
- Semiconductor Quantum Wells and Superlattices
- Magnetic multi-layers and spin valve structures
- LB Plot
- Silicon Inversion Layers in FET

3- DIMENSIONAL NANOMATERIALS (3-D):

All dimensions of these are outside the nanometer range. These include bulk materials composed of the individual blocks which are in the nanometer scale (1-100 nm).
Nanoparticles  Bucky ball

0-DIMENSIONAL

Nanotubes  Nanowires

1-DIMENSIONAL

Nanoplates  Nanolayers

2-DIMENSIONAL

Fig. 1.7 Various dimensions of nanostructures.
Two main factors are considered to determine the properties of NSMs. First, when the grain diameter approaches a few nanometers, the structure modulation length becomes comparable to the characteristic distances of physical processes in solids and the size effects are pronounced. The second important factor is that a significant volume fraction of NSMs is occupied by the atoms at defect sites, mainly in interfaces. Thus, the atomic structure of interfaces is crucial for the properties of these materials. Gleiter classified the NSMs according to the shapes and chemical composition of crystallites. According to the shapes, three categories of NSMs can be distinguished: layer-shaped, rod-shaped, and equiaxed crystallites.

1.3.1 The quantum size effect

When the size of the nanocrystals is smaller than the de-Broglie wavelength, the electrons and holes are spatially confined and electric dipoles are formed in the material, which leads to discrete energy levels of the electronic spectrum of the nanoparticles. This is called as a Quantum size effect.

These changes arise through systematic transformations in the density of electronic energy levels as a function of the size, and these changes result in strong variations in the optical and electrical properties with size. The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the interband transition shifting to higher frequencies.
Fig. 1.8 Schematic illustrating discrete electronic configurations in nanocrystals, nanowires and thin films & enlarged band-gap between the valence and conduction band.
In a semiconductor, the energy separation, i.e., the energy difference between the completely filled valence band and the empty conduction band is of the order of a few electron volts and increases rapidly with a decreasing size. If the size of metal nanoparticle is made small enough, the continuous density of electronic states is broken up into discrete energy levels (Hornyak et al., 2008).

1.4 FABRICATION OF NANOMATERIALS

1.4.1 Outline of synthesis techniques

Synthesis methods for nanoparticles are typically grouped into two categories: “top-down” and “bottom-up” (Fig.1.9). The first involves the division of a massive solid into smaller portions. This approach may involve milling or attrition, chemical methods, and volatilization of a solid followed by condensation of the volatilized components. The second, “bottom-up”, method of nanoparticle fabrication involves condensation of atoms or molecular entities in a gas phase or in solution.

Nanomaterials are made by two generalized processes: Top-down (e.g., subtraction from bulk starting materials) or Bottom-up (e.g., addition of atoms or molecules starting materials, (Karkare et al., 2008)).

1.4.2 Types of top-down fabrication methods:

Nanomaterials are formed from the top down, by (i) mechanical energy, (ii) high-energy, (iii) thermal, (iv) chemical, (v) lithographic, and (vi) natural methods.
Fig.1.9 Types of fabrication processes of nanomaterials.
(i) **Top-down Mechanical-Energy fabrication method**

Cutting, rolling, beating, extrusion, drawing, polishing, compaction, consolidation, machining, milling, and atomization comprises a few examples of mechanical methods used to produce nanomaterials from bulk. A mechanical method employs a physical process that does not involve chemical changes.

(ii) **Top-down Thermal fabrication method**

In the purest sense, a thermal fabrication method employs a physical process (heating) that does not initiate a chemical change in the sample. Nanomaterials are produced from top down mechanical fabrication by Annealing, chill block melt spinning, electro-hydrodynamic atomization (EHDA), electro-spinning, liquid dynamic compaction (LDC), gas atomization, evaporation, extrusion, template synthesis and evaporation, sublimation, thermolysis, pyrolysis, solid combustion, and carbonization of copolymers.

(iii) **Top-down high-energy fabrication method**

High-energy sources such as electric arcs, lasers, solar flux, electron beams, and plasmas are commonly used to produce nanomaterials from the top down. A by-product of high energy methods is superheating: a desirable or undesirable outcome depending on the objectives. Although heat is produced during operation, these are not labeled as thermal methods because of the origin of the heat energy are not a conventional thermal source. There are several commonly used high-energy methods such as arc discharge, laser
ablation, solar energy vaporization, RF sputtering, ion milling, electron beam evaporation, reactive ion etching, pyrolysis, and high energy sonication.

**(iv) Top-down chemical fabrication method**

If chemical transformations occur during a fabrication process, we shall designate that process as a chemical fabrication method. Although fabrication (synthesis) methods that employ chemical procedures rightfully reside within the domain of the bottom up, there are several that can be considered to be top down. Nanometers can be synthesized by various types of chemical fabrications methods such as chemical etching, chemical-mechanical polishing (CMP), electro-polishing, anodizing, and combustion.

**(v) Top-down lithographic fabrication method**

Many powerful top-down techniques involve some form of lithography. Lithographic techniques are what made the integrated circuit industry what it is today, and it continues to be the most viable method to form nanostructures that actually has widespread applications. The classification of lithographic techniques involved in the fabrication of nanostructures are lithographic galvanoformung abformung (LIGA), photo-lithography, immersion-lithography, deep ultraviolet-lithography (DUVL), extreme ultraviolet-lithography(EUVL), X-ray lithography (XRL), electron-beam lithography (EBL), electron beam writing (EBW), electron beam projection lithography (EPL), focused ion beam lithography (FIBL), micro-contact printing method, nano-imprint lithography (NIL), nanosphere lithography (NSL), scanning AFM lithography, scanning probe nanolithography, and 2-photon polymerization.
(vi) Top-down Natural fabrication method

Both the top-down and bottom-up fabrication methods abound in the natural world. Most of these natural processes are quite familiar, and there is no need to allocate any more time or space to them. There are some selected natural processes to provide other relevant fabrication perspectives such as erosion, etching, hydrolysis, volcanic activity, forest and brush fires, solar active, pressure and temperature, biological decomposition, and digestion.

1.4.3 Types of bottom –up fabrication methods:

Bottom-up fabrication techniques are divided into four general categories: (i) gaseous phase methods, (ii) liquid phase methods, (iii) solid phase methods, and (iv) biological methods.

(i) Bottom-up gas-phase fabrication methods

Gases represents highly dispersed phase of atoms and molecules. Some nanomaterials formed in the gas phase, like clusters, remain the gas phase. More commonly, gas-phase precursors interaction with liquid or solid-phase materials. If one of the precursors of nanomaterials originates from the gas phase or if the reaction takes place in the gas phase, we shall call it a bottom-up gas-phase fabrication method. There are several gas-phase fabrication methods such as, chemical vapor deposition (CVD), atomic layer deposition (ALD), thermolysis pyrolysis, metal oxide chemical vapor deposition (MOCVD), organometallic vapor phase epitaxy (OMVPE), molecular beam epitaxy
(MBE), ion implantation, gas phase condensation; thermolysis, and solid template synthesis.

(ii) **Bottom-up liquid-phase fabrication methods**

Bottom-up liquid-phase methods are numerous and diverse. The choice of solvent is an extremely important parameter in any liquid based bottom-up fabrication method. The liquid medium can be hydrophilic or hydrophobic, ionic or anionic, or heterogeneous. Some examples of liquid phase fabrication methods are, molecular self-assembly, supra-molecular chemistry, nucleation and sol-gel process, reduction of metal salts, single-crystal growth, electrodeposition, electroplating, electroless deposition, anodizing, electrolysis in molten salt solutions, solid template synthesis, liquid template synthesis, and supercritical fluid expansion.

(iii) **Bottom-up lithographic fabrication methods**

It is added a special category for lithography once again, but this featuring bottom-up lithographic methods. Bottom-up lithography methods are limited to a few kinds based on template processes or direct writing of examples such as dip-pen nanolithography (DNL), nanosphere template methods, nanopore template method (shadow mask evaporation), block copolymer lithography (BCPL), local oxidation nanolithography, and STM writing. Self-assembled ripple patterns and dot arrays formed by low-energy ion-beam sputtering are another emerging form of bottom-up lithography. Aligned arrays of plasmonic and magnetic wires and nanoparticles are
deposited on these templates via oblique evaporation. The templates are easily produced over large areas with periods down to 25 nm.

(iv) Bottom-up biological and inorganic fabrication methods

Biological processes are overwhelmingly formed from the bottom-up. Some examples are protein synthesis, nucleic acid synthesis, membrane synthesis, inorganic, biological structures, and bio crystal formation methods.

1.5 APPLICATIONS OF NANOMATERIALS

Nanoscience and nanotechnology have become a dominant theme in many research institutions worldwide. A short tour around some of the major development areas in nanoscience and nanotechnology and its applications are given below (Yang et al., 2000).

1.5.1 Smart materials

*Photorefractive polymers*, these highly unusual structures contain mobile electronic charges, almost like metals. The mobile charges can be moved to new positions either by shining light on the polymers or by putting them in an electric field. The position of these charged particles is then a sort of code, a code that can be read by shining different colors of light on the coded polymer, making it work much like a nanoscopic version of a supermarket barcode reader. Photorefractive polymers are of major interest as information storage devices whose storage density can far exceed even the best available magnetic storage structures.
In nanoscience, the term "smart material" refers to any material engineered at the nanoscale to perform a specific task. Photorefractive polymers are particularly complicated and a wonderful form of nanoscale smart materials. Sometimes smart materials are also dynamic, which means that the material can change its most basic properties or structure based on an outside cue. A simple example of a dynamic smart material is self-tinting, automotive glass that is clear most of the time, but darkens under intense light to prevent blinding a driver. In the case of photorefractive polymers, the ability to move charges using light or an electric field is engineered into the material at its most basic level.

1.5.2 Sensors

Sensors are structures that will respond in a recognizable way to the presence of something we wish to detect. There are sensors for temperature, water, light, sound, electricity, particular molecules, and specific biological targets such as bacteria, toxins, explosives, or DNA. Nowadays, researchers are trying to develop sensors by using the properties of molecular recognition. By designing the molecular squares with particular geometries and patterns of molecular electron density the analyte foot fits into the molecular square shoe, but other molecules with different sizes and shapes do not fit. Once the molecular square recognizes and captures the analyte molecule, we must be able to recognize that the capture has in fact taken place, which is usually done by shining light onto the square. The combination of square plus analyte absorbs energy from the light in a different color range (frequency or
wavelength) than the square without the analyte or the analyte alone. This means that if you monitor the sensor, it will change color in the presence of the analyte. These sensors are sensitive enough to detect fewer than 10 molecules of an analyte, so for high-precision tests you might not see the change with the naked eye, but it is not hard to construct lab equipment that can see it. This allows the squares to be among the most sensitive sensors ever made.

Sensor technology is critical to the control and monitoring of the environment.

1.5.3 Nanoscale Biostructure

Action of self-assembly and nanostructures to repair, rather than to remove or replace, parts of human bodies when they run into trouble. A major focus of this research, and a major focus of Nanoscience generally, is so-called nanoscale biostructure. These structures, designed at the nanoscale, can mimic or affect a biological process or interact with a biological entity.

One example of a nanoscale biostructure is provided by a self-assembling "artificial bone," the molecules that make up the bone are held together by chemical bonds. These molecules, in turn, have interactions among them that are weaker than true bonds, but that hold the molecules together with each other in a particular shape, in this case a cylinder. The molecules in the bone are designed to occupy space in a particular way so that they will assemble spontaneously to form the desired shape, and, once assembled, so that they will be packed densely enough for the bone to be very strong. The structure of packed molecules can be made compatible with the human immune system by properly choosing the head groups of the molecule, the
groups of atoms that ultimately form the outer shell of the artificial bone template. The outer shell is also designed so that natural bone begins to form around it like coral on a reef or gold on a piece of plated jewelry. This is key to human repair, allowing the body to fix broken or damaged tissue naturally rather than replacing it with a steel or ceramic implant. Because the biological realm is full of nanostructures, biomedical applications and biomedical investigations constitute a major part of the Nanoscience landscape.

1.5.4 Energy capture, transformation and storage

Industrialized societies require massive amounts of energy, both in continuous supply to homes and businesses and in portable energy for gadgets and personal electronics, the area of energy management comprises one of the major domains of Nanoscience. Major contribution came in the development of something now called the Graetzel cell. In a Graetzel cell, a dye molecule is used to capture the energy from sunlight. The molecule absorbs the light, going into a higher energy state. In this high energy state, the molecule actually separates charge by passing an electron from the dye molecule to a nanoparticle of a white crystal called titanium dioxide, which may be familiar as the pigment material in white house paint.

The separated charges (positive charge remaining on the dye molecule, negative charge shifted to the titanium dioxide nanoparticle) are then allowed to recombine using a set of electrochemical reactions. In this recombination, some of the energy that was originally captured from the sun by the molecule is
released as electrical current passing through an external circuit. Originally, Graetzel cells were used to illuminate bathroom scales and Swiss watches, but they also exemplify a major worldwide effort for capturing sunlight to provide energy sources that are efficient, nonpolluting, safe, and inexpensive. Graetzel cells currently have efficiencies exceeding 7% and can be produced using silk screening techniques, which makes them cheaper to make than most traditional photovoltaic cells.

1.5.5 Optics

Organic light emitting diodes (OLEDs) and all signs of these will be a major technology for illumination in areas from automobile dashboards to room lighting to computer screens. Taking these LED structures down to the nanoscale produces major gains in efficiency, control, cost, and lifetime. Electricity is used to produce light in the light-emitting structures, while light is captured to produce electricity in the photocells. Both are major areas of study in the development of Nanoscience.

1.6 FUEL CELLS

“A fuel cell is an electrochemical device that converts the chemical energy released from a reaction between a fuel and oxidizer directly into electrical energy”.

The fuel cell accomplishes this by separating the overall reaction into two half reactions each occurring on opposite sides on an ion-conducting, electronically insulating membrane.
The two reactions on each side of the membrane are:

1) The oxidation of a fuel at the anode for electron release, and
2) The reduction of an oxidizer at the cathode for electron reception.

The overall reaction involving the oxidation of the fuel can be used to sustain a voltage difference across the membrane and the resulting electronic current flow through an external circuit will produce electrical work.

1.6.1 Basic principle of fuel cells

Fuel cells are electrochemical devices that directly convert chemical energy from a reaction between a fuel and an oxidant into electrical energy. The fuel and oxidant gas flow along the surface of the anode and cathode, respectively, and react electrochemically in the three-phase-boundary region established at the gas/electrolyte/electrode interface. A fuel cell can theoretically produce electrical energy for as long as fuel and oxidant are fed to the porous electrodes, but the degradation or malfunction of some of its components often limits the practical life span of the fuel cell. Different fuels can be used, such as hydrogen, ethanol, methanol, or gaseous fossil fuels like natural gas. Solid or liquid fossil fuels need to be gasified first before they can be used as a fuel. Oxygen or air can be used as an oxidant.

1.7 SOLID OXIDE FUEL CELL

“A solid oxide fuel cell is a device that converts gaseous fuels (hydrogen, natural gas, gasified coal) via an Electrochemical process directly into electricity”.

35
SOFCs are deemed promising as technologies, in terms of overall efficiency, they offer, and their ability to operate with a variety of fuels. Research work under way is addressing definition and development of novel ceramic electrolytes, and specific anode & cathode material, to achieve lower operating temperatures, that enable internal fuel reforming. Such investigations go hand in hand with the development and optimization of material fabrication and forming processes, with the aim of bringing down manufacturing cost. SOFC operates at high temperature (700–1000 °C). Efficiencies as high as 45% have been achieved even though the technology is under development and is not mature at all. By the further technological development, efficiencies higher than 50% are expected. In addition, SOFC emits a high temperature gas that can be utilized for electricity generation by a bottoming cycle. It is reported that the system integrating an SOFC and a gas turbine can achieve an electrical conversion (70%).

1.7.1 Components of SOFC

The four main Components of an SOFC as shown in Fig.1.10, i.e., i) Anode, ii) Cathode, iii) Electrolyte, and iv) Interconnects

1.7.2 Principle

It is based on the diffusion of oxygen ion through the electrolyte from cathode to anode, after ionizing at the air electrode. SOFC is composed of an anode, electrolyte, cathode, and interconnect. Oxidant gas (usually the air) is supplied to the cathode, and the fuel is supplied to the anode. Schematic diagram of the cell is shown in Fig.1.10.
Fig.1.10 Components of SOFC.
The oxidant gas and the fuel are separated by the dense electrolyte. The ionic charge carrier can diffuse in the electrolyte; however, ideally electron and gaseous molecule cannot. In this configuration, the difference of the chemical potential between oxidant gas and fuel is converted to the electrostatic potential difference of the anode and the cathode (i.e., the electromotive force can be obtained). The electromotive force of the single cell is approximately one volt. At the practical operation, there is a voltage loss caused by internal resistance. The voltage loss is called overvoltage, over potential, or polarization. It is important to decrease the over potential in order to enhance the efficiency and output density of the cell.

1.7.3 Working of SOFC

- A fuel cell is like a battery that always runs. It consists of three parts: an electrolyte, an anode and a cathode.

- For a solid oxide fuel cell, the electrolyte is a solid ceramic material. The anode and cathode are made from special inks that coat the electrolyte. Unlike other types of fuel cells, no precious metals, corrosive acids or molten materials are required.

- Next, an electrochemical reaction converts fuel and air into electricity without combustion.

- A solid oxide fuel cell is a high temperature fuel cell. At high temperature, warmed air enters the cathode side of the fuel cell and steams mixed with fuel to produce reformed fuels which enters on the anode side.
• Next, the chemical reaction begins in the fuel cell. As the reformed fuel crosses the anode, it attracts oxygen ions from the cathode. The oxygen ions combine with the reformed fuel to produce electricity, water, and small amounts of carbon dioxide.

\[
\text{Fuel} + \text{steam} \rightarrow \text{Reformed Fuel} \\
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + e^- + \text{Heat}
\]

• The water gets recycled to produce the steam needed to reform the fuel. The process also generates the heat required by the fuel cell.

• As long as there is fuel, air, and heat the process continues producing clean, reliable, affordable energy.

Fig.1.1 showed the working of the two-chamber SOFC. In this type, the fuel and air are supplied to separate chambers. The fuel electrode and air electrode are positioned in the mixed gas of fuel and air is supplied to a single chamber. When the electrolyte is an oxygen ion conductor, oxygen ions are generated from the air electrode in the mixed gas. These ions are conducted through the electrolyte and react with hydrogen at the fuel electrode, producing an electromotive force between the two electrodes (Fergus et al., 2006).
Fig.1.11 operating principles of $O_2^-$ and $H^+$ ion conduction type SOFC.
1.8 MATERIALS AND METHODS FOR SOFC

1.8.1 SOFC materials

The basic components of a ceramic fuel cell stack are the electrolyte, the anode, the cathode and interconnect. Each component serves several functions in the fuel cell and has to meet certain requirements. These requirements include:

- Proper stability (chemical, phase, morphological and dimensional) in oxidizing and/or reducing environments,
- Chemical compatibility with other components and proper conductivity.
- The electrolyte and interconnect must be dense in order to separate the oxidant and fuel gases
- Both anode and cathode must be porous to allow gas transport to the reaction sites.

<table>
<thead>
<tr>
<th>Component part</th>
<th>Main material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Cerate type</td>
</tr>
<tr>
<td></td>
<td>Stabilized zirconia type</td>
</tr>
<tr>
<td></td>
<td>Lanthanum gallate type</td>
</tr>
<tr>
<td></td>
<td>Rare earths doped CeO₂</td>
</tr>
<tr>
<td></td>
<td>YSZ:Y₂O₃ stabilized ZrO₂</td>
</tr>
<tr>
<td></td>
<td>(La, Sr) (GaMg) O₃</td>
</tr>
<tr>
<td>Fuel electrode</td>
<td>Ni/YSZ cermet, Ru/YSZ cermet</td>
</tr>
<tr>
<td>Air electrode</td>
<td>LaMnO₃ type</td>
</tr>
<tr>
<td></td>
<td>LaCoO₃ type</td>
</tr>
<tr>
<td></td>
<td>(La,Sr) MnO₃, (La,ca) MnO₃</td>
</tr>
<tr>
<td></td>
<td>(La,Sr) CoO₃, (La,Ca) CoO₃,</td>
</tr>
<tr>
<td>Separator</td>
<td>LaCrO₃ type</td>
</tr>
<tr>
<td></td>
<td>Alloy type</td>
</tr>
<tr>
<td></td>
<td>(La,Sr) CrO₃, (La,ca) CrO₃</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr type, ferrite (Fe) type</td>
</tr>
</tbody>
</table>

*Table 1.1 Typical component materials of SOFC cells.*
(i) Anode

The anode of state of the art SOFCs is a cermet made of a mixture of various metallic oxide skeletons. The anode has porosity (20-40%) so that mass transport of reactants and product gases is not inhibited. However, there is some ohmic polarization loss at the interface between the anode and the electrolyte and bi-layer anodes have been introduced in order to overcome this problem (often a small amount of ceria is added to the anode cermet; this improves the tolerance of the anodes to temperature and redox cycling).

(ii) Cathode

The Cathode used for an SOFC has to be porous in nature to accommodate and pass the air through and ionize oxygen molecules into ions. The cathode is also a porous structure which must allow rapid mass transport of reactant and product gases. Strontium-doped lanthanum manganite (La$_{0.84}$Sr$_{0.26}$)MnO$_3$, a p-type semiconductor, is the most commonly used material.

(iii) Electrolytes

The electrolytes used in SOFC are highly dense and should be able to conduct protons or Oxygen Ions from cathode to anode. Fast oxide-ion conductors attract considerable interest because of their potential application as electrolyte for a solid oxide fuel cell. Suitable electrolytes for SOFCs must be good purely ionic conductors, permitting the passage of O$_2^-$ ions in the case of a SOFC. Such a cell component must be stable at high temperature and must be easy to synthesize. Required properties of electrolytes are:
• High Ionic Conductivity
• Long Term High Temperature Performance stability
• Density
• High Long Term Reliability

1.8.2 Introduction to cerium (IV) oxide electrolyte

A tremendous momentum has been achieved in nanocrystalline materials for past few years. Since the nanomaterials have large increase in surface area, the efficiency of them increases and undergo wider applications. Such materials show greatly modified optical, electronic, magnetic and other physical properties rather than its bulk materials of the same composition. Recently, rare earth oxide materials play vital role in solid oxide fuel cell (SOFC) electrolyte applications (Inaba et al., 1996; Mogensen et al., 2000; Kharton et al., 2004; Brett et al., 2008). Synthesis of such oxide nanomaterials with enhanced electrical conductivity is achieved by doping of certain rare earth ions such as Gd, Sm, Nd, Er, Pr, Y, Yb, etc.

Ceria is a promising material for intermediate temperature SOFC electrolyte application since it has a high oxygen ion conductivity. It is noted that, the potential of ceria is increased with dopants added to it. It is also accepted that the rare earth doped ceria creates numerous oxygen vacancies which are favourable for higher ionic conductivity than that of undoped ceria (Huang et al., 1997; Steele et al., 2000; Go et al., 2007; Ou et al., 2006; Stephens et al., 2006; Zhan et al., 2001; Fuentes et al., 2009; Yan et al., 2008; Thangadurai et al., 2007).
Number of Energy Levels : 6
First Energy Level : 2
Second Energy Level : 8
Third Energy Level : 18
Fourth Energy Level : 20
Fifth Energy Level : 8
Sixth Energy Level : 2

Fig.1.12 Electronic configuration of CeO$_2$.

Ceria

Ceria unit cell structure

Fig.1.13 Ceria and its unit cell structure.
Therefore doped ceria is a good electrolyte at intermediate-temperature. It must be noted that the ceria based materials have reduced mechanical strength, but the addition of rare earths can slightly improve the mechanical properties (Zhang et al., 2004; Patnaik et al., 2002).

Rare earth doped ceria has the tendency to reduce the functional temperature of SOFC from 1000 °C to 800 °C and acts as good electrolyte. It has been considered as a premium power generation device in future. Cerium (IV) oxide, also known as ceric oxide, ceria, cerium oxide or cerium dioxide is an oxide of the rare earth metal cerium.

1.8.3 Properties of ceria

(i) It is a pale yellow-white powder with the chemical formula CeO₂.
(ii) Cerium (IV) oxide is formed by the calcination of cerium oxalate or cerium hydroxide. (iii) Powdered ceria is slightly hygroscopic and will also absorb a small amount of carbon dioxide from the atmosphere. (iv) Cerium also forms cerium (III) oxide, Ce₂O₃, but CeO₂ is the most stable phase at room temperature and under atmospheric conditions.

1.8.4 Applications of ceria

Cerium (IV) oxide is used in ceramics, to sensitize photosensitive glass, as a catalyst and as a catalyst support, to polish glass and stones, in lapidary as an alternative to "jeweller's rouge". It is also known as "optician's rouge". It is also used in the walls of self-cleaning ovens as a hydrocarbon catalyst during the high-temperature cleaning process. While it is transparent for visible
light, it absorbs ultraviolet radiation strongly, so it is a prospective replacement of zinc oxide and titanium dioxide in sunscreens, as it has lower photocatalytic activity. However, its thermal catalytic properties have to be decreased by coating the particles with amorphous silica or boron nitride. The use of these nanoparticles, which can penetrate the body and reach internal organs, has been criticized as unsafe. Cerium oxide has found use in infrared filters, as an oxidizing species in catalytic converters and as a replacement for Thorium dioxide in incandescent mantles (Patnaik et al., 2002; Green et al., 2009).

(i) As a fuel cell electrolyte: In the doped form (it comes from cerium and oxygen), ceria is of interest as a material for solid oxide fuel cells (SOFCs) because of its relatively high oxygen ion conductivity (i.e. Oxygen atoms readily move through it) at intermediate temperatures (500–800 °C). Undoped and doped ceria also exhibit high electronic conductivity at low partial pressures of oxygen due to the formation of small polarons. However, doped ceria has an extended electrolytic region (area of predominant ionic conductivity), over that of ceria, that allows its use as an electrolyte in SOFCs. Substituting a fraction of gadolinium or samarium or rare-earth ions with ceria will introduce oxygen vacancies in the crystal without adding electronic charge carriers. This increases the ionic conductivity and results in a better electrolyte.

Under reducing conditions, those experienced on the anode side of the fuel cell, a large amount of oxygen vacancies within the ceria electrolyte can be formed. Some of the cerium (IV) oxide is also reduced to cerium (III) oxide under these conditions, which consequently increases the electronic
conductivity of the material. The lattice constant of ceria increases under reducing conditions as well as with decreasing nanocrystal size in nanocrystalline ceria, as a result of reduction of the cerium cation from $4^+$ to $3^+$ state in order to charge compensates for oxygen vacancy formation (Sameer et al., 2005).

**(ii) As a catalyst:** Ceria has been used in catalytic converters in automotive applications. Since ceria can become non-stoichiometric in oxygen content (i.e., it can give up oxygen without decomposing) depending on its ambient partial pressure of oxygen, it can release or take in oxygen in the exhaust stream of a combustion engine. In association with other catalysts, ceria can effectively reduce NO$_x$ emissions as well as convert harmful carbon monoxide to the less harmful carbon dioxide. Ceria is particularly interesting for catalytic conversion economically because it has been shown that adding comparatively inexpensive ceria can allow for substantial reductions in the amount of platinum needed for complete oxidation of NO$_x$ and other harmful products of incomplete combustion.

Due to its fluorite structure, the oxygen atoms in ceria crystal are all in a plane with one another, allowing for rapid diffusion as a function of the number of oxygen vacancies. As the number of vacancy increases, the ease at which oxygen can move around in the crystal increases, allowing the ceria to reduce and oxidize molecules or co-catalysts on its surface. It has been shown that the catalytic activity of ceria is directly related to the number of oxygen vacancies.
in the crystal, frequently measured by using X-ray photoelectron spectroscopy to compare the ratios of Ce$^{3+}$ to Ce$^{4+}$ in the crystal.

Ceria can also be used as a co-catalyst in a number of reactions, including the water-gas shift and steam reforming of ethanol or diesel fuel into hydrogen gas and carbon dioxide (with varying combinations of rhodium oxide, iron oxide, cobalt oxide, nickel oxide, platinum, and gold), in the Fischer-Tropsch reaction, and selected oxidation (particularly with lanthanum). In each case, it has been shown that increasing the ceria oxygen defect concentration will result in increased catalytic activity, making it very interesting as a nanocrystalline co-catalyst due to the large number of oxygen defects as crystallite size decreases at very small sizes, as many as 10% of the oxygen sites in the fluorite structure crystallites will be vacancies, resulting in exceptionally high diffusion rates.

(iii) For water splitting: The cerium (IV) oxide – cerium (III) oxide cycle or CeO$_2$/Ce$_2$O$_3$ cycle is a two step thermochemical water splitting process based on cerium (IV) oxide and cerium (III) oxide for hydrogen production (Mehos et al., 2012).

(iv) Defects: In the most stable fluorite phase of ceria, it exhibits several defects depending on partial pressure of oxygen. The primary defects of concern are oxygen vacancies and small polarons (electrons localized on cerium cations) because these two are located in the "useful" range of ceria. In the case of oxygen defects, the increased diffusion rate of oxygen in the lattice
causes increased catalytic activity as well as an increase in ionic conductivity, making ceria interesting as a fuel cell electrolyte in solid-oxide fuel cells.

1.8.5 Rare earths doped Ceria

The cubic fluorite structured ceria doped with trivalent rare earth elements are considered as very good oxygen ion conductors. Upon doping with trivalent elements in CeO₂ lattice, the oxygen vacancies are created in order to maintain the charge neutrality of the materials. These oxygen ion conducting materials has a wide range of application such as Solid Oxide Fuel Cells, Oxygen pump, Oxygen separation membrane, Oxygen sensor, etc. The dopants such as Nd³⁺, Pr³⁺, Er³⁺, Y³⁺, Gd³⁺ and Sm³⁺ are doped with ceria exhibit the higher ionic conductivity due to small association enthalpy between dopant cations and oxygen vacancy (Anderson et al., 1981; Kilner et al., 1983).

1.9 THE SCOPE OF THE THESIS

The present investigation deals with the synthesis of pure and some rare earth element (La³⁺, Sc³⁺, Yb³⁺, Nd³⁺, Pr³⁺, Er³⁺, and Y³⁺) doped nanocrystalline ceria by citrate nitrate auto-combustion method. Though there are different types of methods of synthesis such as chemical precipitation, hydrothermal, sol-gel synthesis, and other wet-chemical methods; the combustion synthesis provides uniform and size distribution with maximum yield. The present thesis also describes the characterization studies such as structural and morphologies, spectral analyses, mechanical properties, and electrochemical characterizations.