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5. Nanomaterials

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5.1 Introduction:

Today, everybody is talking about nanomaterials, even advertisements for consumer products use the prefix "Nano" as a keyword for special features, and, indeed, very many publications, books, and journals are devoted to this topic. Nanomaterials is a new step in the evolution of understanding and utilization of materials. Material science started with the realization that chemical composition is the main factor in determining what a material is. Hereafter it was discovered that the fabrication and after fabrication steps could influence those properties substantially. Also small additives proved to be able to modify these properties. Finally, with the arrival of nanotechnology, it was discovered that the ability to create small particles could expand the capability to create and modify materials [1,2]. Nanotechnology is as well as evolutionary as revolutionary in nature. Evolutionary are the many applications where the same material is incrementally improved by using nanotechnology. Revolutionary it can be called where new (enabling) properties originate from nanotechnology like for example in quantum dots. Those new properties can be divided in:

- Properties based on the fact that the surface is large compared to the weight/volume.
- In addition to size, low energy dissipation and high processing speeds are important.
- New properties not found in bulk or micro sized particles.

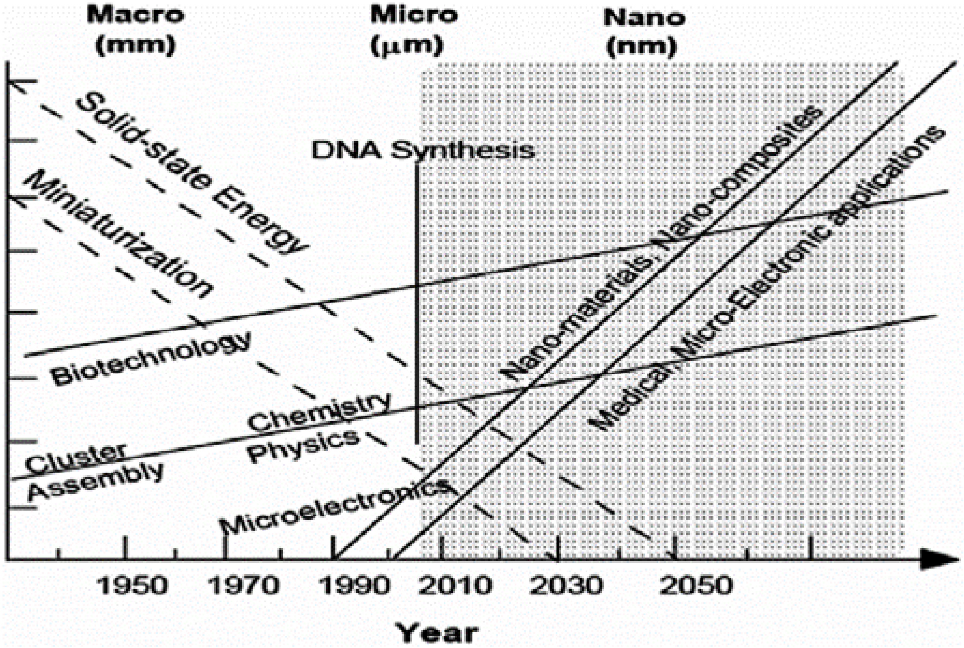

Figure 5.1: Evolution of Science and Technology and The Future

5.2 What Are Nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercials products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.

Engineered nanomaterials are resources designed at the molecular (nanometer) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviour.

5.3 Main Differences Between Nanomaterials and Bulk Materials:

Two primary factors cause nanomaterials to behave significantly differently than bulk materials: surface effects (causing smooth properties scaling due to the fraction of atoms at the surface) and quantum effects (showing discontinuous behavior due to quantum confinement effects in materials with delocalized electrons) [3]. These factors affect the chemical reactivity of materials, as well as their mechanical, optical, electric, and magnetic properties.

5.4 Advances in Nanomaterials:

Today Nano phase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

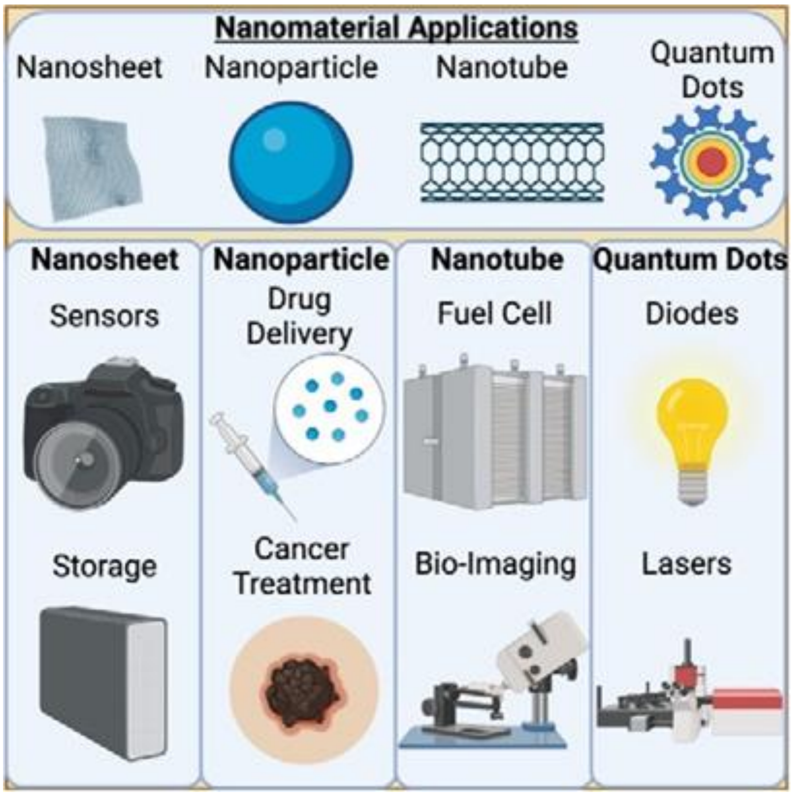

Figure 5.2: Advances in Nanomaterials

5.5 Why Are Nanomaterials Important?

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

- Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.
- Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.
- Nano sized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

5.6 Synthesis of Nanomaterials:

There are a large number of techniques available to synthesize different types of nanomaterials in the form of colloids, clusters, powders, tubes, rods, wires, thin films etc. There are various physical, chemical, biological and hybrid techniques available to synthesize nanomaterials. The technique to be used depends upon the material of interest, type of nanostructure viz., zero dimensional, one dimensional, or two dimensional material size, quantity etc.

- Physical methods: (a) mechanical: ball milling, melt mixing (b)Vapor: physical vapor deposition, laser ablation, sputter deposition, electric arc deposition, ion implantation
- Chemical methods: colloids, sol-gel, L-B films, inverse micelles. Biological methods: bio membranes, DNA, enzymes, microorganisms.

5.6.1 Physical Methods:

a. **Ball Milling:**

It is used in making of nanoparticles of some metals and alloys in the form of powder. Usually the mill contains one or more containers are used at a time to make fine particles. Size of container depends upon the quantity of interest. Hardened steel or tungsten carbide balls are put in containers along with powder or flakes (<50 um) of a material of interest. Initial material can be of arbitrary size and shape. Container is closed with tight lids. The containers are rotated at high speed (a few hundreds of rpm) around their own axis. Additionally, they may rotate around some central axis and are therefore called as 'planetary ball mill'. When the containers are rotating around the central axis, the material is forced to the walls and is pressed against the walls. But due to the motion of the containers around their own axis, the material is forced to other region of the container. By controlling the speed of rotation of the central axis and container as well as duration of milling, it is possible to ground the material to fine powder whose size can be quite uniform.

Some of the materials like Co, Cr, W, Ni-Ti, AlFe, Ag-Fe etc. are made nanocrystal line using ball mill.

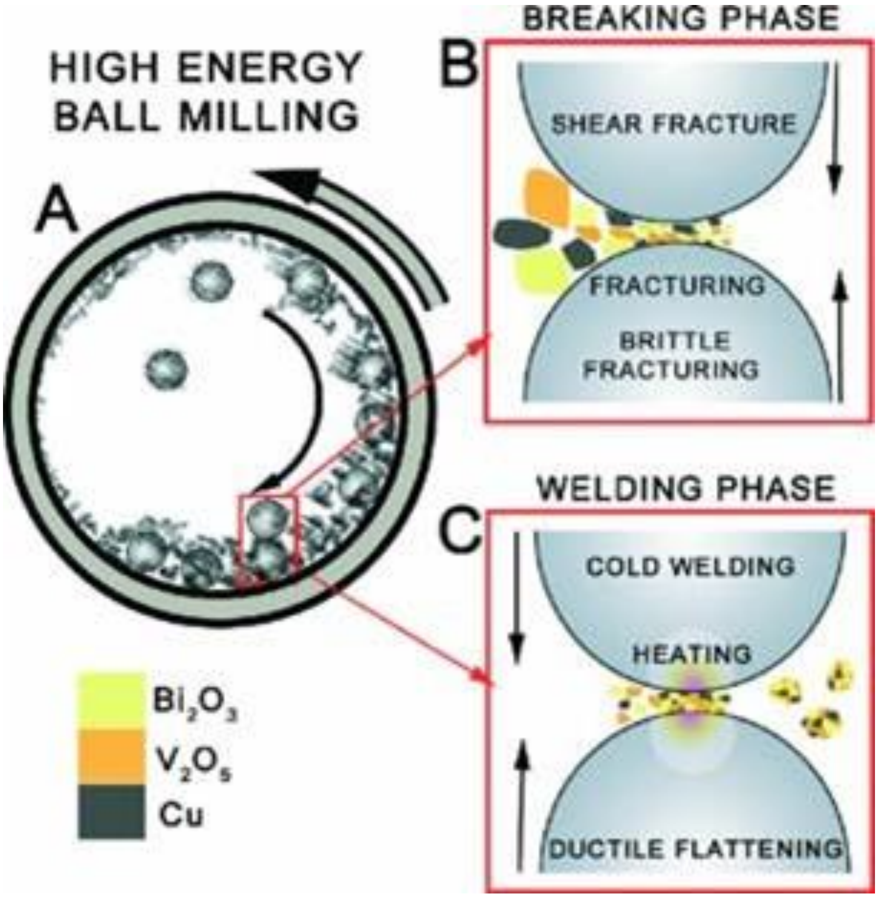

Figure 5.3: Schematic representation of the high energy ball milling synthesis mechanism for Cu- doped $BiVO_4$ nanoparticles

b. **Melt Mixing:**

It is possible to form or arrest the nanoparticles in glass. Structurally, glass is an amorphous solid, lacking long range periodic arrangement as well as symmetry arrangement of atoms/molecules. When a liquid is cooled below certain temperature, it forms either a crystalline or amorphous solid (glass). Nuclei are formed spontaneously with homogenous (in the melt) or inhomogeneous (on the surface of other materials) nucleation, which can grow to form ordered, crystalline solid. Usually, metals form crystalline solids but, if cooled at very high cooling rate, they can form amorphous solids. Such solids are known as metallic glasses. Even in such cases the atoms try to reorganize themselves into crystalline solids. Addition of elements like B, P, Si etc. helps to keep the metallic glasses in amorphous state. It is possible to form nanocrystals within metallic glasses. It is also possible to form some nanoparticles by mixing the molten streams of metals at high velocity with turbulence. On mixing thoroughly, nanoparticles are formed.

c. **Physical Vapor Deposition:**

It involves material for evaporation, an inert gas or reactive gas for collusion of material vapor, a cold finger on which clusters or nanoparticles can condense, a scraper to scrape the nanoparticles and piston- anvil (an arrangement in which nanoparticle powder can be compacted). All the processes are carried out in a vacuum chamber so that the desired purity of the end product can be obtained. Metals or high vapor pressure metal oxides are evaporated or sublimated from filaments or boats of refractory metals like W, Ta, Mo in which materials to be evaporated are held. Size, shape and even the phase of evaporated material can depend upon the gas pressure in deposition chamber. Clusters or nanoparticles condensed on the cold finger (water or liquid nitrogen cooled) can be scraped off inside the vacuum system. The process of evaporation and condensation can be repeated several times until enough quantity of material falls through a funnel in which a piston-anvil arrangement has been provided.

5.6.2 Chemical Methods (Wet Chemical Route):

There are numerous advantages of using chemical methods, which are:

- Inexpensive, less instrumentation compared to many physical methods
- Low temperature (< 350 C) synthesis
- Doping of foreign atoms (ions) possible during synthesis
- Variety of size and shapes are possible
- Self-assembly or patterning is possible

5.6.3 Sol-Gel Method:

As the name implies sol-gel involves two types of materials or components ‘sol’ and ‘gel’. There are several advantages of sol-gel: All sol-gel formation process is usually a low temperature process. This means less energy consumption and less pollution too. Some of the benefits like getting unique materials such as aerogels, zeolites, ordered porous solids by organic-inorganic hybridization are unique to sol-gel process. It is also possible to synthesize nanoparticles, nano rods, nanotubes etc., using sol-gel technique. Sols are solid particles in a liquid. They are thus a subclass of colloids. Gels are nothing but a continuous network of particles with pores filled with liquid (or polymers containing liquid). A sol-gel process involves formation of ‘sols’ in a liquid and then connecting the sol particles (or some subunit capable of forming a porous network) to form a network. By drying the liquid, it is possible to obtain powders, thin films or even monolithic solid. Synthesis of sol-gel in general involves hydrolysis of precursors, condensation followed by polycondensation to form particles, gelation and drying process by various routes. Precursors (starting chemicals) are to be chosen so that they have a tendency to form gels. Both alkoxides or metal salts can be used. Alkoxides have a general formula M(ROH)n, where M is a cation, R an alcohol group, and n is the number of (ROH) groups with each cation. Salts are denoted as MX, in which M is a cation and X is an anion. Although it is not mandatory that only oxides be formed by a sol-gel process, often oxide ceramics are best synthesized by a sol-gel route.

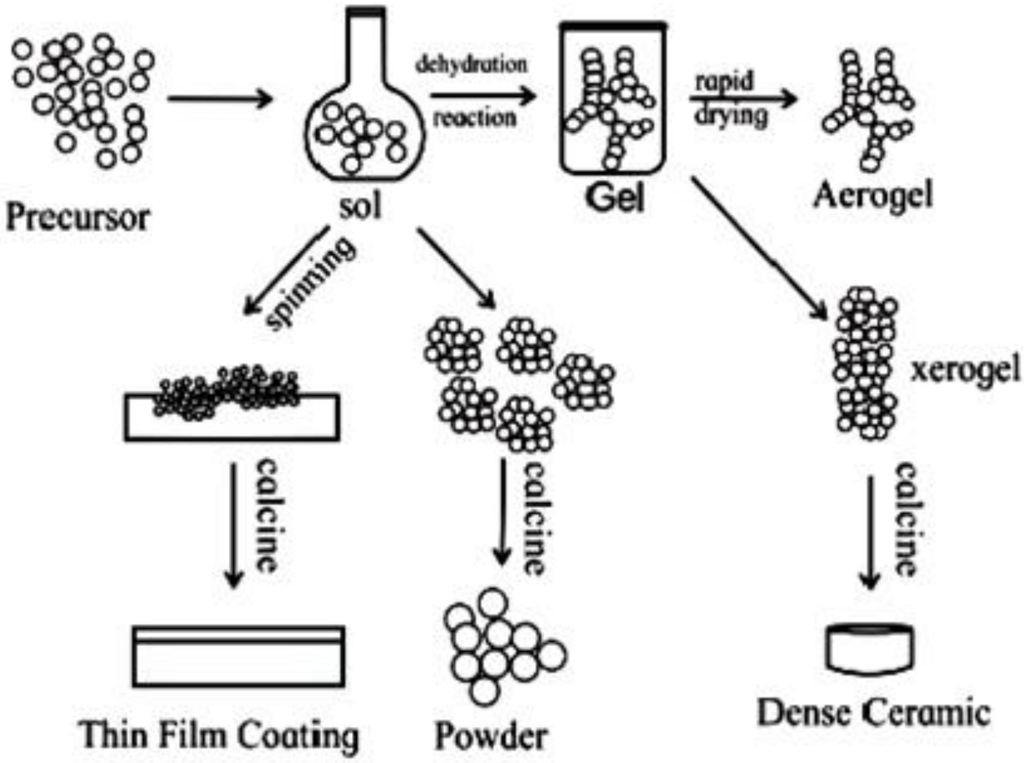

Figure 5.4: Schematic representation of the sol-gel process of synthesis of nanoparticles

a. Colloids and Colloids in Solutions:

A class of materials in which two or more phases (solid, liquid, gas) of same or different materials co-exist with at least one dimension less than a micrometer is known as colloids. Colloids may be particles, plates, or fibers. Nanomaterials are a sub-class of colloids, in which one of the dimensions of colloids is in about 1 to 100 nm range. Colloids are the particles suspended in some host matrix.

b. Microemulsion:

Synthesis of nanoparticles in the cavities produced in micro emulsion is a widely used method. Advantage of this method is the biocompatibility and biodegradability of synthesized materials. Biocompatibility is useful in drug delivery of nanomaterials and biodegradability is environmentally useful. Whenever two immiscible liquids are mechanically agitated or stirred together, they are known to form what is called ‘emulsion’. The tendency of the liquids is such that the liquid is smaller quantity tries to form small droplets, coagulated droplets or layers so that they are all separated from the rest of the liquid (for example droplets of fat in milk). The droplet sizes in emulsion are usually larger than 100 nm up to even few millimeters. Emulsions are usually turbid in appearance. On the other hand, there is another class of immiscible liquids, known as micro emulsions which are transparent and the droplets are in the range of ~1 to 100 nm.

5.7 Unique Nanomaterial Features:

The properties of matter at the nanoscale level are substantially distinct compared to bulk counterparts. Size-dependent effects become more prominent at the nanoscale. For example, Au solution appears yellow when in the bulk and it appears purple or red at the nanoscale level.

The properties of nanomaterials can be tuned via tuning the nanomaterial size.92,93 At the nanoscale, the electronic properties are substantially changed compared to bulk materials.

The electronic properties of semiconductors in the 1–10 nm range are controlled by quantum mechanical considerations. Thus, nano spheres with diameters in the range of 1–10 nm are known as quantum dots. The optical properties of nanomaterials such as quantum dots strongly depend upon their shape and size [4].

Among a range of unique properties, the following key properties can be obtained upon tuning the sizes and morphologies of nanomaterials.

5.7.1 Surface Area:

The surface areas of nanomaterials are generally substantially high compared with their bulk counterparts, and this property is associated with all nanomaterials [5].

5.7.2 Magnetism:

The magnetic behavior of elements can change at the nanoscale. A non-magnetic element can become magnetic at the nanoscale level [6].

5.7.3 Quantum Effects:

Quantum effects are more pronounced at the nanoscale level. However, the size at which these effects will appear strongly depends upon the nature of the semiconductor material [7].

5.7.4 High Thermal and Electrical Conductivity:

According to the nature of the nanomaterial, extraordinary thermal and electrical conductivity can be exhibited at the nanoscale level compared to bulk counterparts. One example of this is graphene attained from graphite [8].

5.7.5 Excellent Mechanical Properties:

Nanomaterials exhibit excellent mechanical properties that are absent in their macroscopic counterparts [9].

5.8 Challenges and Future Perspectives:

Currently, huge numbers of theoretical and experimental literature studies of nanomaterials and nanotechnology have been witnessed. Future technologies depend upon how effectively materials can be manipulated on the nanoscale for various applications. However, at the same time, the development and effective utilization of nanomaterials involve many challenges. The dream of clean energy production is becoming possible with the advancement of nanomaterial based engineering strategies. These materials have shown promising results, leading to new generations of hydrogen fuel cells and solar cells, acting as efficient catalysts for water splitting, and showing excellent capacity for hydrogen storage. Nanomaterials have a great future in the field of nano medicine. Nano carriers can be used for the delivery of therapeutic molecules.

5.9 Conclusion:

In this chapter, the efforts have done to compile the small wonders of nanotechnology and that may be already be in our world and some that may be on the horizon. Nanomaterials are the building blocks of practical nanotechnology and can be physically and chemically manipulated for specific purposes. Nanomaterials play an important role in development of science and technology in various fields such as nano medicine, Nano biotechnology, green nanotechnology, industrial sectors and in reduction of energy consumption. Thus nanomaterials and nanotechnology are the current and future of the technology.

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