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FIRST SLIDE OF E-CONTENT PAGE

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NANOMATERIALS

Nanomaterials are basis of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

Nanomaterials are the particles (crystalline or amorphous) of organic or inorganic materials having sizes in the range of 1-100 nm. Nanomaterials are classified into nanostructured materials and nanophase/nanoparticle materials. The former refer to condensed bulk materials that are made of grains with grain sizes in the nanometer size range while the latter are usually the dispersive nanoparticles. 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. Nanomaterials are chemical substances or materials that are manufactured and used at a very small scale. Nanomaterials are developed to exhibit novel characteristics compared to the same material without nanoscale features, such as increased strength, chemical reactivity or conductivity.

Where are nanomaterials found?

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial 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 (nanometre) 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 behaviours.

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nano coatings and nanocomposites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UVblocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls sing butyl-rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

History of Nanomaterials:

The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many 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 every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibers and catalyst supports. In the 1960s and 1970's metallic Nano powders 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. 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 biocorrosion 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.

Today nanophase 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.

Classification of Nanomaterials:

Depending on the dimension in which the size effect on the resultant property becomes apparent, the nanomaterials can be classified as zero dimensional (quantum dots) in which the movement of electrons is confined in all three dimensions, one-dimensional (quantum wires) in which the electrons can only move freely in the X-direction, two-dimensional (thin films) in which case the free electron can move in the X-Y plane, or three dimensional (nanostructured material built of nanoparticles as building blocks) in which the free electron can move in the X, Y and Z directions. The Variation of density of states with dimensionality for different nanomaterials is shown in Figure-1.





Semiconductor nanocrystals are zero-dimensional quantum dots, in which the spatial distributions of the excited electron-hole pairs are confined within a small volume, resulting in the enhanced non-linear optical properties. The density of states concentrates carriers in a certain energy range, which is likely to increase the gain for electro-optic signals. The quantum confinement of carriers converts the density of states to a set of discrete quantum levels. With consideration the small size of a semiconductor nanocrystal, its electronic properties are significantly affected by the transport of the single electron, giving the possibility of producing single electron devices. The schematic diagram in figure1.1 illustrates the variation of density of states with dimensionality.

Passing from three dimensions to two dimensions the density N(E) of states changes from a continuous dependence N(E) ~ E1/2 to a step like dependence. The optical absorption edge for a quantum well is at a higher photon energy than for the bulk semiconductor and, above the absorption edge, the spectrum is stepped rather than smooth the steps corresponding to allowed transitions

between valence-band states and conduction-band states, while, at each step, sharp peaks appear corresponding to electron-hole (exciton) pair states.

In the case of zero dimensional systems, the density of states is illustrated as a delta function. The low-dimensional structure has proven to be very promising for application to semiconductor lasers, which is mainly due to the quantum confinement of the carriers and the variation of the density of states with dimensionality. The density of states has a more peaked structure with the decrease of the dimensionality. This leads to a reduction of threshold current density and a reduction of the temperature dependence of the threshold current.

Nanomaterials and related devices can be classified into three major categories, and suitable preparative methods are identified depending on the desired resultant structures. The first category of nanomaterials consists of isolated, substrate-supported or embedded nanoparticles, which can be synthesized by physical vapor deposition (PVD), chemical vapor deposition (CVD), inert gas condensation, aerosol processing, precipitation from supersaturated vapors, liquids, or solids etc. Low-dimensional semiconductor structures are usually fabricated by highly sophisticated growth techniques like molecular beam epitaxy (MBE) and metallorganic chemical vapor deposition (MOCVD). Quantum dots can be grown in a relatively easy way via the chemical methods including the colloidal method, sol-gel method, self assembly, embedding in polymers, encapsulation in zeolites or in glasses and so forth. Many terms have been used to describe these ultra small particles, such as quantum dots, Q-particles, clusters, nanoparticles, nanocrystals and others. Usually the zero-dimensional structures prepared in physical methods like MBE and MOCVD are called quantum dots by physicists while the small particles formed in chemical methods are called nanoparticles, nanoclusters, Q-particles or nanocrystallites by chemists The second category refers to materials having a thin nanometer-sized surface layer, which can be processed by techniques such as PVD, CVD, ion implantation, or laser ablation. The major advantage of these techniques is that the processing parameters can be suitably tuned to obtain a nanometer-sized surface layer. The self-organization and chemical self-assembly are also emerging as very important techniques for the deposition of materials layer by-layer with controlled particle size and

composition. Three dimensional (3D) materials having nanometer sized grains belong to the third category. The crucial aspect related to the processing of these materials is control of the chemical composition and the grain size. For example, the metastable 3D nanostructures such as glass, gels, supersaturated solid solutions, or implanted materials can be prepared by quenching the high temperature at equilibrium to the room temperature. The quenching helps to freeze the disordered structure with the composition varying on an atomic scale. Nanostructured-glass ceramics, which belong to the category of metastable 3D nanostructures, have been studied with immense interest in recent years because of the potential engineering applications. Another type of materials that belongs to this group is 3D ordered solid having building blocks as nanocrystals. The microstructures of such solids comprise crystals with varying orientations separated by interfaces, which may be coherent, semi coherent or incoherent. The ideal preparative route for such structures would involve the optimization of the processing conditions to ensure the formation of a microstructure with controlled grain growth so that all the unique properties of the nano building blocks are preserved.