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Nanostructures and their applications

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Abstract

Nanostructures have been described as 'novel materials whose size of elemental structure has been engineered at the nanometer scale'. Materials in the nanometer size range commonly exhibit fundamentally new behavior. Moreover, intervention in the properties of materials at the nanoscale enables the creation of materials and devices with enhanced or completely new characteristics and functionalities. Understanding the science of nanomaterials is important and curiosity driven not only because of the fascinating nature of the subject but also for overwhelming and novel applications of nanoscale systems in almost all branches of technology.Nanotechnology can be understood as a technology of design, fabrication and application of nanostructures and nanomaterials.The field of nanoscience and nanotechnology is interdisciplinary in nature and it is being perused by physicists, chemists, materials scientists, biologists, engineers, computer scientists etc. Nanomaterials may be classified on the basis of dimensionality and modulation. Some special nanostructures like nanotubes, nanoporous materials, aerogels, zeolites, core-shell structures have also come up with their novel characteristics. A number of methods have been used for the synthesis of nanostructure with various degrees of success and many direct and indirect techniques are employed for their characterization. The fact, which makes the nanostructures interesting, is that the properties become size dependent in nanometer range because of surface effect and quantum confinement effect. The geometric structure, chemical bonds, ionization potential, electronic properties, optical properties, mechanical strength, thermal properties, magnetic properties etc. are all affected by particle sizes in nanometer range. Nanomaterials exhibit properties often superior to those of conventional coarse-grained materials. These include increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density, reduced elastic modulus, higher electrical resistivity, increased specific heat, higher thermal expansion coefficient, lower thermal conductivity, increased oscillator strength, blue shifted absorption, increased luminescence and superior soft magnetic properties in comparison to conventional bulk materials. All of these properties are being extensively investigated to explore possible applications. The fascinating field of nanotechnology has wide range of applications. Use of nanostructutred materials has produced transistors with record low speed and lasers with low threshold current. These are being used in compact disk player systems, low noise amplification in satellite receivers as sources for fiber optic communication etc. Constructive applications of nanomaterials include self-cleaning glass, UV resistant wood coating etc. Nanoscale devices are being used in medical field also for diagnosis, treatment and prevention of diseases and in drug delivery system, magnetic resonance imaging, radioactive tracers etc. Importance of nanotechnology is growing day by day. Many more applications may be possible with the novel and peculiar properties of nanostructures.

Keywords: Nanostructure, Nanomaterials, UV resistant wood coating

INTRODUCTION

Nanostructures have been described as 'novel materials whose size of elemental structure has been engineered at the nanometer scale'. Dictated by the demands of miniaturization, increasing efforts are being made to synthesize, understand and apply the materials with reduced dimensions. The interest in nanomaterials is growing at a dramatic rate due to realization that reduced dimensions in nanometer regime can alter and improve the properties of materials. Nanomaterials have attracted widespread attention since 1990s because of their specific features that differ from bulk materials. This has opened up with tailor-made materials enormous possibilities to meet challenges in different disciplines like medicine, biotechnology, optoelectronoics, engineering etc. of new, effective and efficient devices, drugs or tools. It is expected that the emerging technology will focus on challenges of miniaturization and energy saving, covering different technologies that are existing today. It is therefore not very surprising to see that scientist from different disciplines are joining hands to contribute to this dynamic growing field of nanomaterials.

Definition

The origin of the term 'nano' comes from Greek word for 'dwarf' but in scientific jargon 'nano' means 10^{-9}. So a nanometer means a billionth of a meter, that is 10 times the diameter of hydrogen atom or approximately 1/10000 of the diameter of human hair. Nanotechnology can be understood as a technology of design, fabrication and application of nanostructures and nanomaterials. The concept of nanotechnology, however, dates back to the history of the famous lecture that Noble Laureate Richard Feynman gave in 1959: The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. Later Drexler expanded Feynman's philosophical thinking in a most stimulating manner in 1960, in his book: "Nanotechnology is the principle of manipulation atom by atom, through control of structure of matter at molecular level. It entails the ability to build molecular systems with atom by atom, yielding a variety of nanomechanics". Chemistry deals with the study of atoms and molecules, a realm of matter whose dimensions are generally less than 1 nm, while solid state physics deals with matter of essentially an infinite array of bound atoms or molecules of dimensions greater than 100 nm. A significant gap exists between the two regimes, which is mesoscopic or intermediate regime of nanostructures from 1 to 100 nm or approximately 10 to 10^6 atoms or molecules per particle.. In this nanoscale regime neither quantum chemistry nor classical laws of solid state physics holds and the matter exhibits new size dependent properties. Such materials have come to be known as nanomaterials.

Changes in Properties

All the materials- may be metals, semiconductors or insulators- have size dependent physico-chemical properties below a certain critical size depending upon the details of the materials. For most of the materials, it is below 100nm. Thus geometrical structure, chemical bonds, ionization potential, electronic properties, optical properties, mechanical strength, melting point, magnetic properties etc. are all affected by the particle sizes.

a) *Mechanical properties:* It has been observed that nanocrystalline materials have reduced elastic modulus and density by 30% or less. This may be due to large free volume at interfacial space and increased average inter-atomic distance. Hardness or strength increases by 4-5 times with decreasing size. Diffusivity of nanomaterials also increases up to double of the initial. Numerous interfaces provide paths for diffusion. Increased diffusivity increases sinterability at lower temperatures.

b) *Thermal properties*: It is found that melting point is lowered with decreasing particle size. It may be reduced to half of the original. The specific heat and thermal expansion may increase up to 50% or more with reducing particle size.

c) *Optical properties*: The color and transparency of materials change by changing the size of nanoparticles. Hence these can be controlled by processing parameters. Due to the increase in effective band gap of materials, absorption spectra shift towards higher energy and for small particle; it may show stepwise absorption by decreasing size of nanocrystals. Enhanced luminescence with fast response has been observed by decreasing size of nanocrystals; this is because of changes in electronic structure and useful in fast response devices with emission of desired color. Nanoparticles may be used in lasers also since these can operate at lower threshold. Confinement of photons and phonons in nanoparticles also affect the Raman spectra. Nonlinear optical properties are also observed in semiconductor clusters in glass or polymer matrix.

d) *Magnetic Properties*: Saturation magnetization values of nanoparticles are smaller but coercive values are much larger than their polycrystalline counterparts because of their high surface to volume ratio and increased effective anisotrophy. Curie temperature of ferromagnetic materials decreases with decreasing size of nanoparticles, and hence the substance remains paramagnetic even below usual Curie temperature showing super paramagtetism. In nanocrystalline phase, each particle is a single ferromagnetic domain.

e) *Electrical properties:* Electrical properties are also affected by the size in nanometer range. Electrical conductivity is reduced by decreasing the size of nanocrystals. Ferroelectric materials (e.g.$PbTiO_3$) become non-ferroelectric at reduced sizes (20 nm). Transition temperature of superconducting materials (e.g.$YBa_2Cu_3O_7$) is reduced and these become non-superconducting for smaller sizes.

This has opened up a huge possibility of synthesising and manufacturing the materials with desired characteristics. It should be noted that for a particular material there is always a critical size below which properties are size dependent. In these materials the length of reduced dimension has to be smaller than the phase coherent length or the mean free path scattering length for electrons in the materials.

Reasons for novel properties

Nanomaterials exhibit properties often superior to those of conventional coarse-grained materials and in addition, the properties can be tailored by controlling the size. The changes in the properties of nanomaterials are driven mainly by three factors:

a) *Increase in surface area to volume ratio:* Atoms and molecules at surface or interface have different environment and bonding configuration, therefore these exhibit different characteristics. In micron size particles, the fraction of surface atoms is less than 10^{-8} and so they cause little effect. As size is reduced, relative number of atoms on surface increases inversely as particle size. For small sizes of the order of few 100 nm, the fraction of surface atoms is large and therefore influences the properties by greater amount making the properties size dependent.

b) *Quantum size effect:* When the size of the particle is comparable to phase coherent length of electrons, the energy spectrum is quantized into discrete levels. The effect is observable for particle sizes of the order of few 10 nm. In case of metals the continuous energy levels are discretized with energy spacing E_f/N, where E_f is Fermi energy and N is number of electrons present. The discretization in energy levels is experienced when their spacing exceeds the thermal energy. Quantum size effect is more pronounced in semiconductor nanoparticles because of moderate forbidden energy gap. Quantum size effect makes the energy states at the edges of valence and conduction bands forbidden, increasing the effective band gap, which affects the electronics and optical properties.

c) *Lattice contraction:* At very small sizes of the order of a few nm, lattice parameters may be reduced because of inward inter-atomic forces. Structural phase change, such as from cubic to hexagonal, has also been observed in this size range.

Intervention in the properties of materials at the nanoscale enables the creation of materials and devices with enhanced or completely new characteristics and functionalities.Therefore these find wide applications in various devices and improved performance is achievable and with the help of these materials .certain new novel devices have also become possible.

Classification

Interestingly, the reduction in the physical size of the materials may be only in one direction, giving rise to a thin film or reduction may be in two dimension making it wire or reduction may be in all direction making it a point. This puts certain restrictions on the motion of charge carriers. It is not difficult to visualize that for a bulk (3-D) material charge carriers are free to move in all directions; whereas for a plainer material or thin film (2-D), charge carriers are confined only in a plane. The charge carries in a wire or 1-D material will be allowed to flow only in one direction; whereas charge carriers inside a cluster, nanoparticle or quantum dot (0-D) are confined in a very small region in space. This gives rise to quantum confinement and most of the properties like electrical conductivity, optical absorption, thermal conductivity etc. depend on the electronic structure and vary due to this effect. The effect occurs when the dimension is of the order of phase coherent length of electrons. Siegel has suggested on elegant method of categorizing nano-phased materials in terms of modulation dimensionality (μ). In general, nanostructured materials are modulated over length scales of a few nm in zero, one, two or three dimensions – in addition to usually being spatially confined below 100 nm in one or more of these dimensions. Isolated clusters can be thought to have $\mu = 0$ (unmodulated), multilayers have $\mu = 1$ (i.e. modulated only in the direction normal to the layers), ultra fine grained over layers have $\mu = 2$, while compacted nanomaterials have $\mu = 3$.

Synthesis

It is a great challenge to synthesize particles of nanometer dimensions with narrow size distribution and purity. A variety of methods are used to obtained nanostructured material. In principle, any method capable of producing very fine grain sized polycrystalline material can be utilized to produce nanocrystalline materials. Currently there are two approaches: reducing the size, also known as *top down* approach and building up by self-assembly or *bottom up* approach to obtain nano–size materials. In top down process larger materials are reduced to smaller dimensions of the order of nanometers and in bottom-up approach the materials are build-up to nanometer size. The commonly used methods can be categorized as physical and chemical methods.

Physical method:

a) Consolidation
b)Gas aggregation of monomer
c)Inert gas evaporation
d) Sputtering
e) Ion beam method
f) Ball milling g) Lithography

Chemical methods:

a) Chemical precipitation and capping
b) Sol-gel method
c)Micro-emulsion
d) Condensed phase synthesis
e) Reduction technique
f) Electro-chemical deposition

Whatever be the method of synthesizing the nanoparticles, it is essential to avoid the coalescence of particles into larger particles and achieve monodispersity and chemical stability over a long period. Therefore the synthesis routes which protect or passivate the particles have become attractive compared to those which do not take care of long term stability or monodispersity.

All the above mentioned methods are used with different levels of success to produce nanocrystalline phases in a variety of materials. Usually gas condensation, mechanical alloying and chemical precipitation technique have been most commonly employed to produce nanocrystallites; while vapour deposition, sputtering and electrodeposition techniques have been used to synthesize the layered nanocrystals. The sol-gel process is generally used to produce clusters. Gas condensation and mechanical alloying are most commonly employed to produce large quantities of nanocrystallites.

Characterization

In order to understand the inter-relationship between structure and properties, nanocrystalline materials need to be characterized on both atomic and nanometer scales. The characteristic of above involves determining the shapes and sizes of nanoparticles and understanding of the inter-particle interactions. This information is important both from the scientific and the industrial application point of view. A number of experimental techniques have been employed to yield structural information on nanocrystalline materials. These include 'direct' microscopic techniques such as: -

a) Atomic force microscopy (AFM)
b) Transmission electron microscopy (TEM)
c) Scanning electron microscopy (SEM)
d) Field ion microscopy (FIM)

In addition to these, many indirect techniques are also used to obtain the information about the nanomaterials indirectly. A few indirect techniques are: -

a) Absorption spectra
b) Diffraction of X-rays, electrons or neutrons
c) Rutherford back scattering (RBS)
d) Raman spectroscopy
e) Auger electron spectroscopy (AES)
f) Photoluminescence and Photoluminescence excitation

X-ray diffraction patterns for various sizes of nanocrystals show that the peaks are broadened as the crystal size is reduced. The absorption edge or peak is shifted towards higher energy side by reducing the size indicating the widening of the forbidden energy gap of the material. These techniques are complementary to each other. Depending on the system to be studied, one technique may be better than the other.

Special Nanomaterials

With the advancement in technology, it has become possible to synthesize and characterize certain new types of materials having very small dimensions and novel characteristics. Nanomaterials are made by arranging the atom regularly at nanometer scale. This has given rise to certain special materials like fullerenes, carbon nanotubes, nanoporous materials, dendrimers, aerogels, zeolites, core–shell structure etc.

a) *Fullerenes :* These are very large molecules of carbon having, 60, 70 or more atoms on the surface of nearly spherical cage like structure. These forms face centered cubic structure. It is possible to trap some ions inside the fullerene cage or attach some functional molecules to fullerene from outside. Due to their small size, these can be used for drug delivery.

b) *Carbon Nanotubes (CNTs):* These can be considered as cylinders made of graphite sheets, mostly closed at ends. The thickness of sheet is just the atomic size of carbon atom and area about a few square micrometers. It is also possible that many concentric cylinders may form as a nanotube. Such nanotubes are termed as multiwall carbon nanotube (MWCNT). The distance between their walls is 0.334nm. These are more common, however under certain conditions it is possible to obtain single wall carbon nanotube (SWCNT). CNT have a great technological application in electronics, optoelectonics, drug delivery etc.

c) *Porous Silicon:* Materials become porous when some solid particles are removed from them leaving voids in them. The properties of porous materials are quite different. Silicon is very widely used in electronics, but not much useful for optoelectronics due to its indirect band gap. Porous silicon with nano-size pores becomes direct band material and light emission is obtained from this in visible range. The nanosized pores in silicon wafers can be produced by chemical eteching, ion irradiation etc. This is useful for optical and electrical devices. Emission wavelength can be tuned by pore size.

d) *Aerogels:* Aerogels constitute another class of highly porous materials. These ultra low density materials are formed by inter connection of particles of nanometer size to form nano porous material. Pores themselves are usually non-uniform with sizes from ~ 10 to 100 nm. These materials are synthesized by sol-gel method and dried by specialized procedure to retain their porous structures. Aerogel formation of various materials such as silica, alumina, gelatin, cellulose and many others substances have been successfully demonstrated. These posses many interesting properties because of their highly porous structure. They are lightest materials synthesized having pore diameter of few tens of nm with 2-5 nm size particles (80-90 % porous). These have low density (.003 to .08 g/cm^3), high surface area, low refractive index, low speed of sound through them, (~20 m/s), low Young's modulus and very low thermal conductivity (.003 W/m.k). Due to their special properties these find application as thermal insulators in jackets, blankets etc., sound proof rooms, filters for gaseous pollutants etc.

e) *Zeolites:* Porous silicon and aerogels have disordered pores of irregular shapes and sizes. Zeolites are highly ordered porous materials. These have small pores (>2 nm) of uniform size which are periodically arranged to have long range order. The pore sizes can be controlled. The material is crystalline and useful to carry out different reactions. Tetrahederal units of Si and Al connected with Si- O- Al bonds is example of zeolites. These are useful catalysts or absorption materials. It is possible to synthesize and organize nanoparticles inside zeolites.

f) *Core shell particles:* Core- shell particles form a novel class of nanocomposite materials in which a thin layer of nanometer size is coated on another material by some special procedure. The core can be just a nanoparticles (a few nm) with a nanometer thick coating or it can be a large core (few 100 nm) with nanometer thick coating. The Properties are different for core or shell materials. These usually depend on core to shell ratio. Core shell particles can be synthesized using variety of combination of dielectrics, metal, semiconductor, dye, biomolecules etc. Core particles of different morphologies such as rods, rings, cube etc. also can be coated with thin shell. These can be utilized for creation of quantum bubbles (hollow sphere with thin shells).Core- shell structures are used for chemical stability, enhanced luminescence properties, engineering band structure, sensors, drug delivery etc.

Applications

Because of the very fine grain sizes, nanocrystalline materials exhibit a variety of properties that are different and often considerably improved in comparison with those of conventional coarse-grained polycrystalline materials. The fascinating field of nanotechnology has wide range of applications. Use of nanoscale materials may improve the performance of presently available devices. The nano-version of silica, titanium dioxide, clays, powdered metals, polymers and chemical products will be established in near future. New materials with difference performance characteristics may also be developed from nanostructured materials. On the other hand some new products have come up such as nanotubes, bucky balls, dendrimers, quantum dots etc. which are at research level.
A few of the applications are mentioned below:

i) *Tougher and harder cutting tools*: Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide, and titanium carbide, are much harder, much more wear-resistant, erosion-resistant, and last longer than their conventional (large-grained) counterparts. They also enable the manufacturer to machine various materials much faster, thereby increasing productivity and significantly reducing manufacturing costs. Also, for the miniaturization of microelectronic circuits, the industry needs microdrills with enhanced edge retention and far better wear resistance. Since nanocrystalline carbides are much stronger, harder, and wear-resistant, they are currently being used in these microdrills.

ii) *Ductile, machinable ceramics*: Ceramics are very hard, brittle, and difficult to machine. These characteristics of ceramics have discouraged the potential users from exploiting their beneficial properties. However, with a reduction in grain size, these ceramics have increasingly been used. Zirconia, a hard, brittle ceramic, has even been rendered superplastic, i. e., it can be deformed to great lengths (up to 300% of its original length). However, these ceramics must possess nanocrystalline grains to be superplastic. In fact, nanocrystalline ceramics, such as silicon nitride (Si_3N_4) and silicon carbide (SiC), have been used in such automotive applications as high-strength springs, ball bearings, and valve lifters, because they possess good formability and machinabilty combined with excellent physical, chemical, and mechanical properties. They are also used as components in high-temperature furnaces. Nanocrystalline ceramics can be pressed and sintered into various shapes at significantly lower temperatures, whereas it would be very difficult, if not impossible, to press and sinter conventional ceramics even at high temperatures.

iii) *Phosphors for high-definition TV & flat-panel displays* : The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel technique are candidates for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render high-definition televisions (HDTVs) and personal computers affordable to be purchased by an average household. Also, the flat-panel displays constructed out of nanomaterials possess much higher brightness, contrast and fast response than the conventional ones owing to their enhanced electrical and magnetic properties.

iv) *Optical filters and attenuators*: Optical transparency of nanocrystalline ceramics can be controlled by grain size. By changing the size optical filters for different colors can be made. These are also useful for sunscreens etc.

v) *Lasers with low threshold current* : Double heterostructure lasers made from quantum well and quantum dots can be operated at extra low threshold current, which are used in compact disk players optical communications etc.

vi) *Elimination of pollutants*: Nanocrystalline materials possess extremely large grain boundaries relative to their grain size. Hence, nanomaterials are very active in terms of their of chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

vii) *High-power magnets*: The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains) of the grains. It has been shown that magnets made of nanocrystalline yttrium-samarium-cobalt grains possess very unusual magnetic properties due to their extremely large surface area. Typical applications for these high-power rare-earth magnets include quieter submarines, automobile alternators, land-based power generators, motors for ships, ultra-sensitive analytical instruments, and magnetic resonance imaging (MRI) in medical diagnostics.

The emerging fields of nanoscience and nanoengineering are leading to unprecedented understanding and control over the fundamental building blocks of all physical things. Importance of nanotechnology is growing day by day because of its advantages in almost all fields like electronics, computers, medicine, engineering, defense etc. in addition to pure sciences. Nanoparticles nanotubes, nanofibres are changing today's technology because of their size dependent properties. Nanoporous materials are also playing an important role in nanotechnology because of some unusual characteristics. Many more applications may become possible in future due to novel and peculiar properties of nanostrcurues.

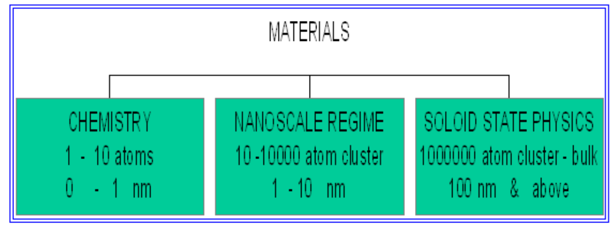

Fig 1. Size relationship of Chemistry, Nanoparticles and Solid state physics

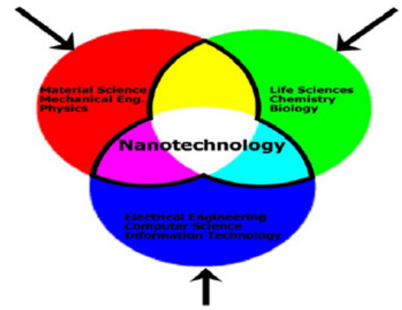

Fig 2. Intersection of Scientific Disciplines

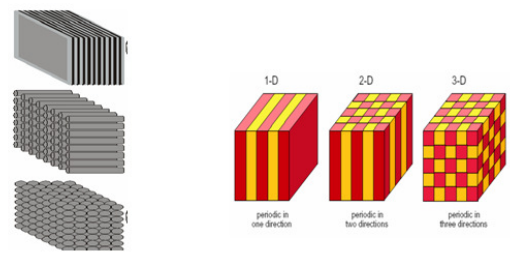

Fig 3. Scaling down Materials : Degree of confinement

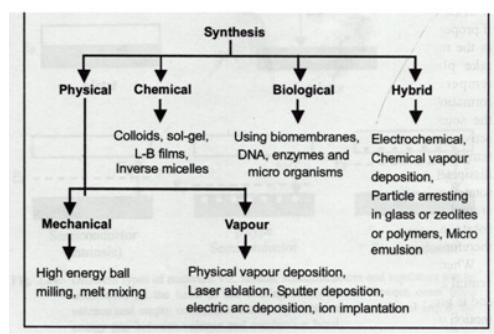

Fig 4. Methods of Synthesis

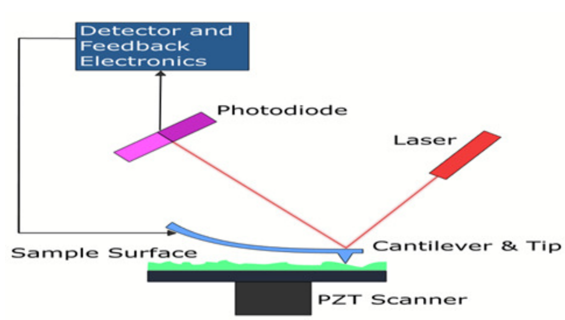

Fig 5. Atomic Force Mircoscopy

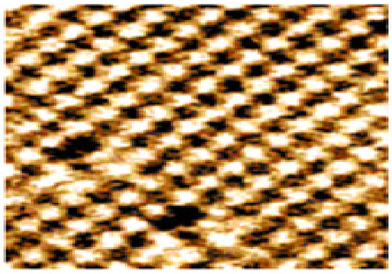

Fig 6 (a). AFM image of NaCl

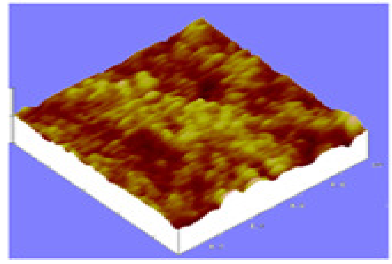

Fig 6 (b). AFM of ZnS:Mn nanoparticles

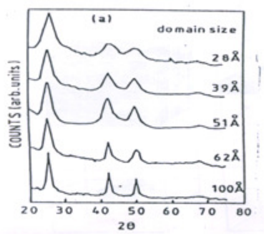

Fig.7 XRD of InAs nanoparticles

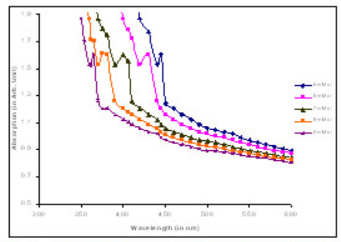

Fig.8 Absorption Spectra CdSe Nanoparticles

Fig. 9 Aerogels

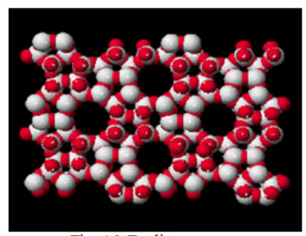

Fig. 10 Zealites

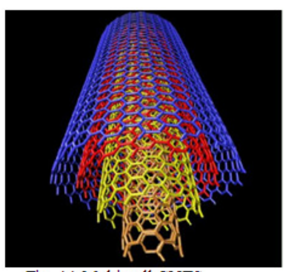

Fig. 11 Multiwall CNTS

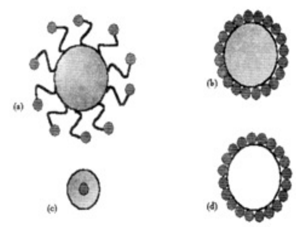

Fig. 12 Core-Shell Structures

Fig.13.Fluorescence of CdSe Nanoparticles of different sizes under UV Light

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