

Recent trends and developments in nanomaterials

L. Robindro Singh

Department of Physics, Pachhunga University College, Aizawl 796001, India
E-mail: robindro001@yahoo.co.in

Why the research journals, magazines, newspapers even literate and illiterate society talk about nanoscience and nanotechnology? Why every addresses of our former President of India, A.P.J. Kalam had advised to the scientific community to promote nanoscience and nanotechnology in our country? Why huge packages were announced in the past years to promote nanoscience and nanocenters in India? Developed and developing countries had already opened new courses, departments and nanocenters especially for nanoscience. Why the peoples are so interested and eager in this field of science? A brief account on the development of nanoscience and nanotechnology is reported in this article.

History of Nanotechnology

The past couple of decades, research in the nanoscience and nanotechnology is one of the thrust areas in all branches of science. The basic reason is their intriguing novel physical and chemical properties of the matters compared to their bulk counterparts. Nanotechnology encompasses the production of physical, chemical and biological systems at scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a profound impact on our economy and society in the early twenty-first century, comparable to that of semiconductor technology or cellular and molecular biology.

Science and technology researches in nanotechnology promise breakthrough in areas such as materials and manufacturing nanoelectronics, medicine and healthcare, energy, biotechnology, information compared to their bulk counterparts. It is widely felt that nanoscience will

be the next industrial revolution. While the word nanotechnology comes, we have to define the term nanoparticle. The research and product of nanoparticle is so advanced and a numbers of publications have also been published, though there is no exact definition of this term.

The word nano comes from the Greek work *nanos* which means dwarf, designates a milliards (10^{-9}) fraction of a unit. The science of nanostructures and nanomaterials deals with objects in condensed matter physics on a size scale of 1 to 100 nm. Nanoparticles can be defined as the size of matters having one or more dimension of the order of 100 nm or less (Fig. 1). The number of atoms or molecules comprising in a nanoparticle so far reported is about 10^4 to 10^6 . As few number of atoms or molecules comprise in the particle the optical, electrical and magnetic properties of the materials are altered when the bulk particles become in these size regime. One of the peculiar examples is that the band gap of semiconductor nanoparticles are increased with the reduction of sizes to few nanometer sizes, leading to the change in the optical and electrical prop-

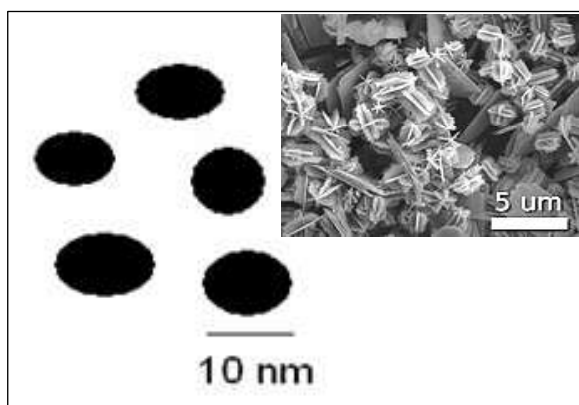


Fig. 1. Nanoparticles [Inset: SEM of nanostars of vanadium (IV) oxide]

erties of these materials. Nanoparticles are the bridges between the atoms or molecules and bulk of the materials. Thus, study of nanomaterials will lead to the miniaturization of industry in coming years.

The special physical properties of small particle have been utilised by peoples for a long time, although these have been carried out unknowingly. Suitable examples are ancient Egypt glasses, coloured with colloidal particles of metals, dye pigments used in different historical periods. In Roman period, colloids metals were used to dye glass articles, cups, fabrics and as a therapeutic aid in the treatment of arthritis. In glass, many noble metal colloids/sols are impregnated and depending on sizes of colloids, different colors were observed. The Lycurgus cup was used in 4th century AD. Now, it is preserved in the British Museum in London. This appears red in transmitted light and green in reflected light. This arises due to the presence of Au and Ag colloids in the walls of the glass cup.

The first scientific mention of small particles is evidently the disordered movement of flower pollen particles, suspended in a liquid, discovered in 1827 by Scottish botanist R. Brown. This phe-

nomenon is referred to as Brownian motion. The article on this microscopic observation laid foundations to many investigations. The theory of Brownian motion, independently developed by A. Einstein and M. Smoluchowski at the beginning of the 20th century is the basis of the one of the experimental methods of determining the size of small particles.

The starting point of examination of the nanostructured state of substance was the investigations in the area of colloid chemistry, which were already quite extensive since the middle of the 19th century. At the beginning of the 20th century, a significant contribution to the experimental confirmation of the theory of Brownian motion, to the development of colloid chemistry and examination of dispersed substances, and to the determination of the size of colloid particles was provided by the Swedish scientist T. Svedberg in 1919. He developed a method of separating colloid particles from a solution using an ultracentrifuge. In 1926, he received a Nobel Prize in chemistry for his work on dispersed systems.

The 20th century is characterised by extensive investigations of heterogeneous catalysis, ultrafine powders and thin films. These investigations raise questions about effect of the small size of particles (grains) on the properties of the studied materials. At present, the nanostructured materials include nanopowders of metals, alloys, intermetallics, oxides, carbides, nitrides, borides and these substances in the bulk state with the grains of the nanometer size, together with nanopolymers, carbon nanostructures, nanoporous materials, nanocomposites, and biological nanomaterials.

The development of nanomaterials is directly associated with the development and application of nanotechnology. The examination of nanomaterials has revealed a large number of grey

areas in the fundamental knowledge of the nature of the nanocrystalline state and its stability under different conditions. On the whole, the field of nanomaterials and nanotechnology is very wide and at present has no distinctive contours. Nanomaterials can be amorphous or crystalline. If nanoparticles are crystalline, they are considered as nanocrystalline or nanocrystal materials. These are related to the many branches of sciences and engineering and can be considered as interdisciplinary subject.

In 1857, Michael Faraday carried out the preparation of colloidal noble metals using reducing agent. He quoted as “Gold is reduced in exceedingly fine particles which becoming diffused, produced a beautiful fluid – the various preparation of gold whether ruby, green, violet or blue – consists of that substance in metallic divided state.” In 1905, Albert Einstein explained in his paper the Brownian motion of colloidal particles in solution. Many scientists neglected the importance of colloidal particles in that time. In view of this, Oswald published a book on “*The World of Neglected Dimensions*” in 1915.

Importance of miniaturization of particles/substances came after a famous lecture series by Ri-



Fig. 2. Feynman

chard Phillips Feynman in 1959 (Fig. 2). He was a joint recipient of the Nobel Prize in Physics for the development of quantum electrodynamics in 1965, together with J. Schwinger and S.-I. Tomonaga. His talk is popularly known as top-down nanotechnology: There is plenty of Room at the Bottom – How do we write small – I do not expect that such prizes will have to wait very long for claimants. His lecturer series came to original importance in nanotechnology. Until 1980, most scientists used the small particles as fine particles. Renowned scientist, H. Gleiter (Fig. 3) published a review article on nanocrystalline materials in 1989. This review article comprised of many works related to nanomaterials published by scientists in the world. This review article is most cited today. Recently, Gleiter had delivered an invited talk on “Are there ways to produce materials beyond the limitations of today?” in 8th International Conference on Nanostructured Materials, August 20-25, 2006, IISc, Bangalore, India and this gives the hint for coming up another system in material science.

The first theoretical explanation of the quantum confinement effect of zero dimensional nanomaterials or quantum dots comes after Efros and Efros in 1982, successfully explains changing of band gap of the particles depending on the sizes of the particles. The novel properties and potential applications of these materials have drawn the interests of many researchers in recent years. Special attention is paid to nanocrystalline semiconductors for their remarkable properties such as nanoelectronics, quantum electronics, sensor technology, non-linear optical and solar technology, different from their conventional counterparts. It is believed that in this decade the highest number of scientific publications and books come from nanoscience and nanotechnology.

Since the last decades in India also investigat-



Fig. 3. Glieter

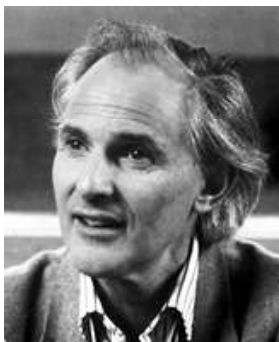


Fig. 4. Kroto

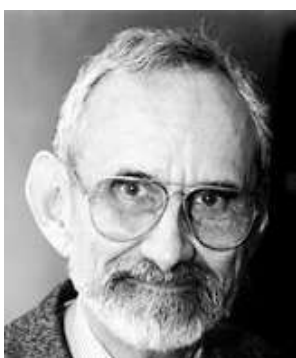


Fig. 5. Curl

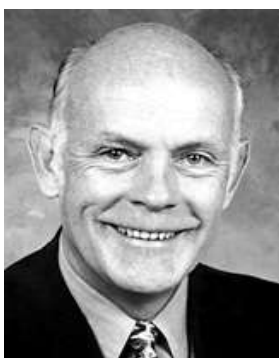


Fig. 6. Smalley

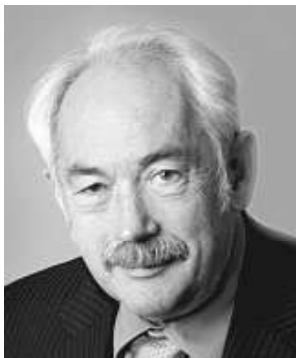


Fig. 7. Grünberg



Fig. 8. Fert

ing on the nanoparticles some prominent investigators are Prof. N. S. Gajbhiye at IIT Kanpur started nanocrystalline materials in ferrites, garnates, nitrides and metals, Prof. C. N. R. Rao at JNCSR, Banglor started nanomaterials in carbon nanotubes, nitrides, oxides, sulphides. Simulation and theoretical investigations of the novel properties of these low dimensional mate-

rials are carried out in the institutes like IISc. Banglore, IITs, Prof. A. K. Sood, D.D.Sharma of IISc. Banglore, Prof. A.N. Shrinivas, Prof. K. Choudhury of IIT Guwahati, etc. and even some of the Indian universities are also developing various departments and courses of this science.

Some of the scientists who got Nobel Prize for works related to nanomaterials are:

1. Fullerene: In 1985, Harold Kroto, James R. Heath, Sean O'Brien, Robert Curl and Richard Smalley, from Rice University, discovered C_{60} , and shortly thereafter came to discover the fullerenes. Kroto (Fig. 4), Curl (Fig. 5), and Smalley (Fig. 6) were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of this class of compounds.

2. GMR: Giant Magneto-Resistance (GMR) was discovered in 1988 in Fe/Cr/Fe trilayers by a research team led by Peter Grünberg (Fig. 7) in Germany and Albert Fert (Fig. 8) in France. Each layer has a few angstroms to 5 nm. This is one of breakthroughs in nanotechnology. The discovery of GMR is considered the birth of spintronics in which both the spin and the charge of electrons can be exploited. Giant magnetoresistance can be used by the read-out head that scans the hard disk and converts the magnetic information into electrical current. Both shared the Nobel Prize in Physics in 2007.

In 1991, there was a discovery of carbon nanotubes (Fig. 9) that it brought carbon nanotubes into the awareness of the scientific community as a whole. A carbon nanotube is one of allotropes of carbon. For this, a few scientists namely S. Iijima, (1991, Japanese), T. Ebbesen (1993, Japanese) and P. M. Ajayan (1993, Indian) may get Nobel Prize in near future.

At present and future, we can challenge nanotechnology in different aspects of life: 1) energy technologies, 2) transportation, 3) informa-

tion technology, 4) biotechnology, 5) robotics, 6) material science, 7) cosmetic technology, 8) nuclear energy, 9) alternative source of fuel (H_2) produced from various processes such as splitting of H_2O , and 10) space science and technology, etc. We have to include importance of nanomaterials as a new subject in schools, colleges, universities and institutions.

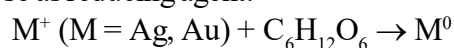
Synthesis of Nanomaterials

The prime importance of the study of nanoparticle is their synthesis with controlling the sizes. Controlling the sizes and resists the agglomeration of the particle is the task of preparation of nanoparticles, as the properties of the particles are changed depending on the size of the particle. The synthesis of nanomaterials can be divided in to (1) chemical and (2) physical methods.

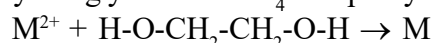
1. Chemical methods

(a) Reduction route

Noble metals can be prepared by using glucose as reducing agent.



Fe, Co and Ni can also be prepared by using ethylene glycol or $NaBH_4$ or superhydride.



Similarly, metal alloys/ composites can be prepared.

(b) Sol-gel route

Metal alkoxides are used as precursors. The solution of metal alkoxides is heated at 80-90 °C for 12 h under reflux condition. It will give sols and is then allowed to evaporation to get gel. The gel is heated to higher temperature to obtain pure metal oxides. M_xO_y and ferrites can be prepared.

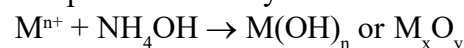
(c) Citrate-gel route

Metal ions are reacted with citric acid to produce metal citrate. It is refluxed for 12 h and then

allowed to evaporation to get jelly mass. The gel is heated to higher temperature to get pure metal oxides. M_xO_y and ferrites can be prepared through this route.

(d) Precipitation route

Metal ions can be reacted with NH_4OH or urea to produce metal hydroxide or oxide.

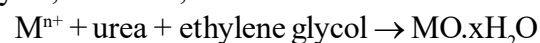


Metal sulphides are prepared by treating metal ions with thiourea/ Na_2S as source of S^{2-} .



(e) Using capping agent

In most cases of (a-d), agglomeration of smaller particles occurs. This can be avoided using capping agents such as citric acid, ethylene glycol, oleic acid, etc.



(f) Microemulsion

To get self-assembly nanoparticles, microemulsion route can be used. In this, surfactant, oil and water are used to make nanoreactor where the formation of metals, oxides and sulphide occurs. The process is also known as reversed micelle route. Particles are in water medium and surrounded by surfactant molecules. van-der Waal and Coulombic repulsion forces develop between micelles. Because of this, particles are distant apart to form self-assembly.

(g) Solvothermal route

In solvothermal route, solvent with reactant species are put into a sealed vessel such as Teflon vessel. It is heated above the normal boiling point of solvent. The pressure is generated in the vessel due to elevation of the boiling point of the solvent. It is like as pressure cooker. If the solvent is water, it is known as hydrothermal. Many nanoparticles such as oxides, sulphides, and metals can be prepared.

There are many other routes such as (h) Photochemical route, (i) Gamma-ray irradiation route,

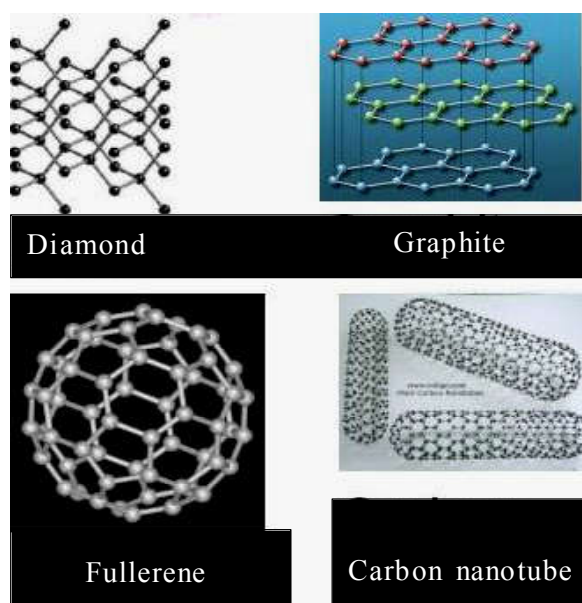


Fig. 9. Allotropes of carbon

(j) Electrochemical route, (k) Single molecule precursor route, (l) Sonochemical route, (k) green chemistry route, (l) core-shell formation route, etc.

2. Physical methods

(a) Gas condensation

In gas condensation, a metal foil or ingot is heated in a ceramic crucible placed in a chamber filled with an inert gas, typically a few torr of argon. When metal atoms evaporate and contact with surrounding inert gas. Exchange in energy takes place and metal atoms cool down and form metal nanoparticles. Different densities of nanoparticles can be obtained after applying different pressures on nanoparticles. Depending on surrounding gases, metal oxides, sulphides and nitrides can be obtained.

(b) Ion sputtering

In ion sputtering, accelerated ions such as Ar^+ are directed toward the surface of a target such as metal plate to eject atoms and small clusters from its surface. The ions are transported to the sub-

strate such as Si under a relatively high pressure (~ 1 mTorr) of an inert gas. Method is also known as sputtering technique. Metal, metal alloys and semiconductors can be prepared.

(c) Laser ablation

In laser ablation, a suitable pulsed excimer laser is used to evaporate the metal or oxide target. In this, nanoparticles can be deposited on the substrate.

(d) Pyrolysis

(i) Chemical vapor pyrolysis: In this, a suitable gas is passed over the metal or metal oxide or metal molecules at high temperature, metal, oxide, nitrides or sulphide nanoparticles can be obtained. If CH_4 gas passed over the benzene, different allotropes of carbon such as graphite, carbon nanotubes can be obtained.

(ii) Spray pyrolysis: In this, small droplets of a solution containing a desired precursor are injected into the hot zone of a furnace and nanoparticles can be prepared.

There are also other methods to prepare nanoparticles like (e) Ball milling, (f) Arch discharge, (g) Molecular beam epitaxy (MBE), (h) Microwave route, (i) Sonochemical route, etc.

Characterization

The prepared nanoparticles are characterized by the following phenomena:

1. X-ray diffraction

The average crystallite size (t) of the materials is calculated from x-ray diffraction line broadening by using Scherrer relation

$$t = 0.9\lambda / B \cos\theta, \quad (1)$$

where, t = average diameter of the crystallites, B = broadening of diffraction line measured at half of its maximum intensity in radians, and $B^2 = |B_m^2 - B_s^2|$ where B_m and B_s are the measured breadth

of the diffraction lines of the sample and the standard samples say Si or Al_2O_3 . In this equation, the particles are assumed as spherical.

2. BET surface area measurement

In BET (Brunauer, Emmet and Teller) surface area measurement, 0.1 g of the material is mounted in the BET tube and all the gases present are removed. Helium gas is passed through the tube for a few hours and it acts as the carrier gas. Now, N_2 gas is passed through the tube at liquid nitrogen temperature. N_2 gas is adsorbed over the surface of ultrafine particles and amount of adsorbed N_2 over the surface per gram weight of the sample give the surface area. Assuming the particles to be spherical in dimension, the diameter (d) will give the particle size from the equation

$$d = 6 / \rho_d S_a, \quad (2)$$

where, ρ_d is the density of the sample and S_a is the surface area per gram of the sample.

3. Electron microscopy

The particle size, morphology and size distribution of materials is studied using electron microscopy: SEM (scanning electron microscopy) and TEM (transmission electron microscopy). In this, high energetic beam of electrons (a few KeV) falls into samples. Some part of electrons or secondary electrons is reflected (in the case of SEM), some part is transmitted through sample if sample is thin (in the case of TEM) and a remaining energy is absorbed by sample. Fig. 10 shows the Co nanoparticles separated by surfactant.

4. Atomic force microscopy

The surface topography study of materials is carried out using atomic force microscopy (AFM). The laser light falls over the top of cantilever that has tip of nanodimension. Cantilever

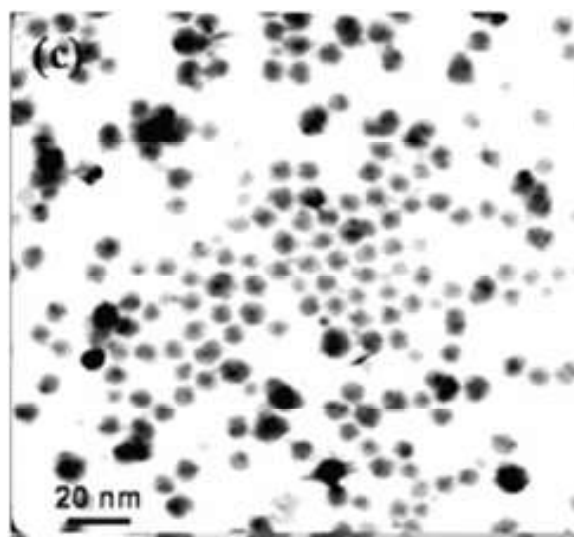


Fig. 10. TEM images Co nanoparticles

can move over the surface of material. This technique has the advantages like the higher resolution (atomic scale), no surface charging and the operation without vacuum environment, even in liquid medium not affecting the sample. The cantilever oscillation frequency and the spring constant are equal to the resonance frequency and the force constant, respectively. The vertical features are characterized by the root mean square roughness (Z_{rms}) and computed by the following discrete approximation (for a two-dimensional $N \times N$ image where pixel heights are h_j): $Z_{\text{rms}} = \sqrt{\{1/N^2 \sum_{i=1}^N \sum_{j=1}^N (h_j - h_{\text{av}})^2\}}$. Nowadays, AFM instrument has many features like MFM (magnetic force microscopy) and scanning tunneling electron microscopy (STEM).

There are many other methods to characterize nanoparticles are HRTEM, EXAFT, SANS, SAXS, DLS, electrical resistivity, magnetization, calorimetry, specific heat, etc.

Properties

1. Bonding

Atom consists of nucleus and electrons. When two atoms come together, the repulsion and attractive forces arise resulting in bonding (BMO) and antibonding (AMO) molecular orbitals separated by an energy gap (ΔE_1). When another third atom is close to them, energy gap between BMO and AMO (ΔE_2) decreases, i. e., $\Delta E_1 > \Delta E_2$. With further addition of atoms, energy gap decreases. It makes cluster of atoms/molecules. With further increase of atoms in cluster, it can come to nanoparticles. In case of semiconductors, additional discrete energy levels will develop near the conduction and valence bands before reaching to bulk. The energy gap in nanostructured semiconductor is more than that in bulk. Thus, it is known as quantum confinement in semiconductor. In case of metals, low conductivity of electrons is found in nanomaterials compared to the bulk value. Schematic diagram shows the formation of semiconductor gap through atom, molecules and clusters (Fig. 11).

2. Surface/core atomic density

Cluster of 13 atoms contains 12 atoms on the surface, regardless of the packing scheme followed. Nanoparticles have high surface atoms. One 1 nm size particle has 50:50 atomic densities

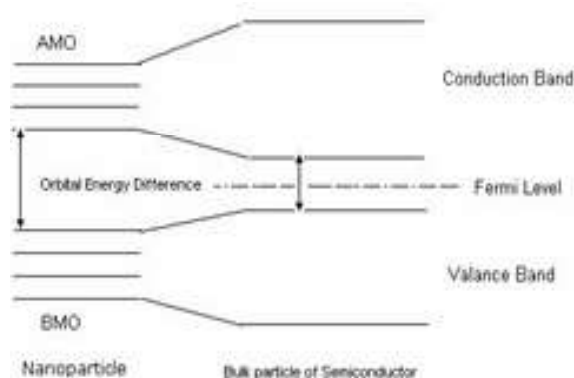


Fig. 11. Energy levels in semiconductors

for surface to bulk ratio. Here, atoms are considered as hard sphere model. The fraction of atoms on the surface of the particle (P_s) can be predicted as

$$P_s = 400 / \sqrt[3]{N} \quad (3)$$

where, N is total number of atoms in the particle. Usually, nanoparticles have 10^4 - 10^5 atoms.

3. Optical study

In metal nanoparticles, there are free electrons over surface of particle. It shows the surface plasmon band in visible region in the electronic absorption spectra due to interaction of the electric field component of the light wave with the dipolar oscillation of the electrons. This was explained in 1908 by G. Mie. It is most prominent when particle diameter (d) is less than the wavelength (λ) of incoming light. The extinction co-efficient of absorption (C_{ext}) is given by

$$C_{ext} = \frac{24\pi^2 d^3 \epsilon_m^{3/2}}{\lambda} \times \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2} \quad (4)$$

where ϵ_1 and ϵ_2 are the real and imaginary part of the frequency-dependent dielectric constant and ϵ_m is dielectric constant of the surrounding medium. Absorption co-efficient becomes maximum when $\epsilon_1 = -2\epsilon_m$.

Metal nanocrystals of various sizes exhibit characteristic colors depending on their diameters and dielectric constant of the surrounding medium. Usually, noble metal nanoparticles (Au, Ag) show the significant band shift with variation of particle sizes.

In semiconductor nanoparticles, number of free electrons is much less than that of metal. So, plasmon absorption band is shifted to the infra-red region. Instead, excitonic transition takes place in UV-visible region. The particle size dependent on exciton band was explained by Brus in 1983

based on the effective mass approximation. Excitons are imaginary quasiparticles produced by pairing of an electron (from the conduction band) and a hole (from the valence band), due to Coulombic interaction. Exciton forms H like atom states with diameter significantly larger than the unit cell length. The exciton radius (R_b) can be related as

$$R_b = \frac{\hbar^2 \epsilon}{e^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad (5)$$

where, m_e^* and m_h^* are the effective masses of electron and hole, respectively. ϵ is dielectric constant of medium. \hbar and e are the Planck's constant and electronic charge, respectively. When the particle radius (R) is less than or equal to R_b , the blue shift in absorption band occurs. Otherwise, absorption band is similar to that of bulk. The band gap of nanoparticle semiconductor (E_g) is more than the bulk ($E_{g(R \rightarrow \infty)}$) due the quantum confinement effect (QCE). It is given by

$$E_g = E_{g(R \rightarrow \infty)} + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad (6)$$

Exciton band in semiconductor is important in luminescence because it absorbs electrons significantly and electrons go to higher excited state; and thus semiconductor can exhibit efficient luminescence. Fig. 12 shows the efficient luminescence for Eu^{3+} doped SnO_2 dispersed in Y_2O_3 when excited through exciton band.

4. Magnetisation

The magnetic properties of fine particles are attractive for theoretical and practical studies. These have finite size effects in the range of 3-20 nm. Their properties differ from those of the bulk because with decreasing particles size, a fraction of the total magnetic atoms at the surface increases. The electronic and magnetic structure of

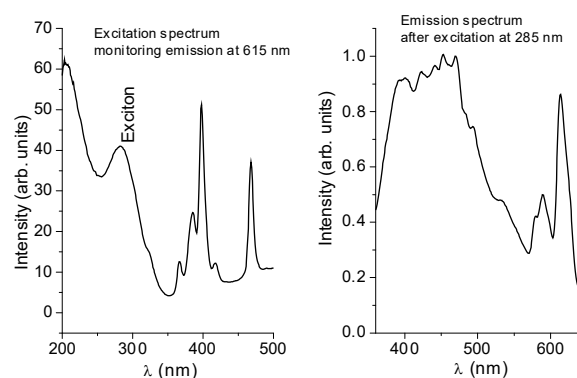


Fig. 12. Excitation and emission spectra of $\text{SnO}_2:\text{Eu}-\text{Y}_2\text{O}_3$

these atoms is modified due to the smaller number of neighbours as compared to the bulk, and/or by the interaction with the surrounding atoms of the matrix where the particles are dispersed. These are called nanoparticles or nanocrystalline materials. Magnetic nanoparticles are also good candidates for the study of quantum effects in intermediate scales between the microscopic and macroscopic classical world.

The crystalline magnetic materials can be divided into two: 1) single domain particles having uniform magnetization. These are particularly fine particles whose particle size is smaller than the exchange correlation length or critical size. 2) multi-domain particles having non-uniform magnetization. These are larger size particles.

For magnetic behaviour of an assembly of non-interacting fine particles with uniaxial anisotropy, thermal energy ($k_B T$, where k_B is the Boltzmann constant and T , the temperature) at the temperature is sufficient to equilibrate the magnetization of an assembly of fine particles in a short time compared to that of the experiment. There will be a tendency with the decrease in particle size towards a state where the particle magnetization has random directions. Here the magnetic anisotropic energy (KV , K is the anisotropic constant depending on the electronic structure, shape,

stress and size of the particles having volume V) is smaller than the thermal energy ($k_B T$). This will happen when particle size is less than the critical particle size at a particular temperature. The magnetic behaviour of such particles is called superparamagnetism.

The superparamagnetic particles have the relaxation time (τ_0) where the particles behave as paramagnetic character but have large moment. The superparamagnetic relaxation (τ) can be described by the Arrhenius-Neel expression

$$\tau = \tau_0 \exp(KV/k_B T) \quad (7)$$

The value of τ_0 depends on the gyromagnetic precession time and is usually equal to 10^{-10} - 10^{-13} s. In Mössbauer spectroscopy, the superparamagnetic relaxation results in line broadening for the relaxation time of the order of 10^{-8} s and for $\tau \leq 10^{-9}$ s, the magnetic hyperfine splitting for the ferromagnetic material disappears, and paramagnetic spectra with one or two lines (doublet) appears. Superparamagnetic particles follow the classical Langevin paramagnetism. In single domain region, as particle size decreases, the coercivity (H_c) decreases because of thermal effects as

$$H_c = g - h/D^{3/2}, \quad (8)$$

where, g and h are constants. Below the critical size (D_c), H_c tends to zero due to thermal effects. Such particles show the superparamagnetic behaviour. For fine particles, there is a temperature called Blocking temperature, T_B . Below T_B , the magnetization will be stable (magnetic moments are blocked in a fixed direction). For uniaxial particles, T_B is

$$T_B = KV/25k \quad (9)$$

Above T_B , fine particles exhibit superparamagnetic behaviour. T_B is determined from both magnetization measurements and Mössbauer studies. Typically, blocking temperature, (T_B) is well below the Curie temperature and

therefore, the magnetization density of each particle approximately remains constant up to T_B . From the zero field cooled (ZFC) and field cooled (FC) studies in magnetic- dc and ac susceptibility (c) measurements, T_B can be calculated. Above T_B , the ZFC and FC curves merge each other, indicating that the sample exhibits superparamagnetism.

The effective magnetic moments of ultrafine ferromagnetic particles are usually found to be below the bulk values. It gives an idea of change in the magnetic nature of fine particles because there are surface atoms that are different from the core. The ultrafine particles may be visualized as having a core with the normal spin arrangement and the surface layer in which the spins of ions/atoms are not oriented at random; but are inclined at some angles to their normal direction depending on their magnetic nearest neighbors. Fig. 13 shows the decrease of magnetization (σ) with decrease of particle size in Co nanoparticles.

The Curie temperature (T_c) is a characteristic of ferromagnetic particles. T_c value decreases with decrease of particle size. The particle size dependence (D) of the T_c compared to the bulk value can be explained by using scaling equation as

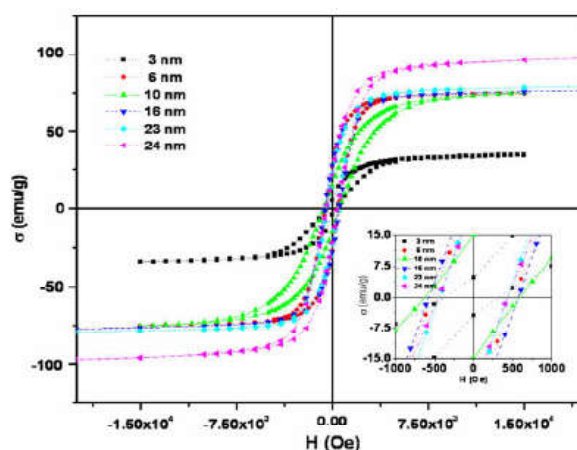


Fig. 13. σ vs. H for Co nanoparticles

$$[(T_c(D) - T_c(\text{bulk})) / T_c(\text{bulk})] = \pm (D/D_0)^{-\lambda} \quad (10)$$

where $\nu = 1/\lambda =$ correlation length. The D_0 is the order of the characteristic microscopic dimension of the system.

5. Electrical resistivity

The electrical resistivity increases with decrease of particle size. In small particle size system, contribution of resistivity comprises of both bulk and surface/grain boundary.

Applications

Because of small particles in nanomaterials, they are used in many applications: (a) gas-sensing, (b) catalyst, (c) tracer in biology, (d) drug-delivery, (e) optical devices, (f) magnetic memory, etc. One of the breakthrough works in magnetic memory is the discovery of 100 Terabyte 3.5-inch Digital Data Storage Disks (Fig. 14) by Michael E. Thomas.

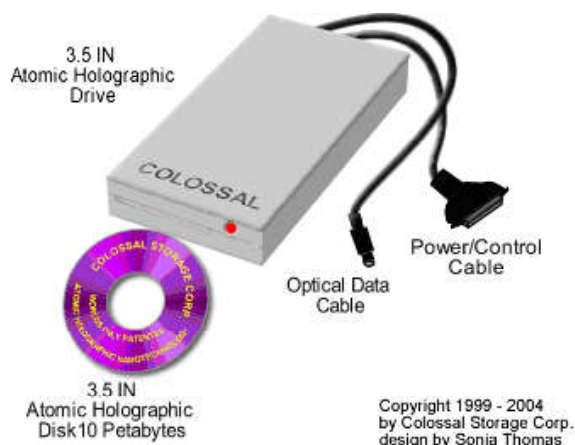


Fig. 14. 100 Terrabyte 3.5 inch disk

References

1. Efron AL & Efron AL (1982). *Phys Semicond Sov*, **16**, 772.
2. Ningthoujam RS, Sudhakar N, Rajeev KP & Gajbhiye NS (2002). Electrical resistivity study of La, B doped nanocrystalline superconducting vanadium Nitride. *J Appl Phys*, **91**, 6051.
3. Ningthoujam RS, Sudarsan V, Godbole VS, Tyagi AK, Kienle K & Kulshreshtha SK (2007). SnO₂:Eu³⁺ nanoparticles dispersed in TiO₂ matrix: Improved energy transfer between semiconductor host and Eu³⁺ ions for the low temperature synthesized samples. *Appl Phys Lett*, **90**, 173113.
4. Ningthoujam RS, Gajbhiye NS, Ahmed A, Umre SS & Sharma SJ (2008). Re-dispersible Li⁺ and Eu³⁺ co-doped ZnO nano-dumbbell: Luminescence and EPR studies. *J Nanosci Nanotech*, **8**, 3059.
5. Singh LR, Ningthoujam RS, Sudarsan V, Srivastava I, Singh SD, Dey SK & Kulshreshtha SK (2008). Luminescence study on Eu³⁺ doped Y₂O₃ nanoparticles: particle size, concentration and core-shell formation effects. *Nanotechnology*, **19**, 055201.
6. Singh LR, Ningthoujam RS, Sudarsan V, Singh SD & Kulshreshtha SK (2008). Probing of surface Eu³⁺ ions present in ZnO:Eu nanoparticles by covering ZnO:Eu core with Y₂O₃ shell: Luminescence study. *J Lumines*, **128**, 1544-1550.
7. Singh NS, Ningthoujam RS, Devi LR, Yaiphaba N, Sudarsan V, Singh SD, Vatsa RK & Tewari R (2008). Luminescence study of Eu³⁺ doped GdVO₄ nanoparticles: Concentration, particle size and core/shell effects. *J Appl Phys*, **104**, 104307.
8. Gajbhiye NS, Sharma S, Nigam AK & Ningthoujam RS (2008). Tuning of single to multidomain behavior for self-assembly ferromagnetic cobalt nanoparticles. *Chem Phys Lett*, **466**, 181.

9. Rao CNR, Thomas PJ & Kulkarni GU (2007). *Nanocrystalline: Synthesis, Properties and Applications*. Springer-Verlag, Berlin Heidelberg, Germany.
10. Gleiter H (1989). Nanocrystalline materials. *Prog Mater Sci*, **33**, 223.
11. Kroto HW, Heath JR, O'Brien SC, Curl RF & Smalley RE (1985). C₆₀: Buckminsterfullerene. *Nature*, **318**, 162.
12. Iijima S (1993). Helical microtubules of graphitic carbon. *Nature*, **354**, 56; Iijima S & Ichihashi T (1993). Single-shell carbon nanotubes of 1-nm diameter. *Nature*, **363**, 603; Ebbesen TW & Ajayan PM (1992). Large-scale synthesis of carbon nanotubes. *Nature*, **358**, 220.
13. <http://www.its.caltech.edu/~feynman/plenty.html>
14. Grünberg P, Schreiber R, Pang Y, Brodsky MB & Sowers H (1986). Layered Magnetic structures: evidence for antiferromagnetic coupling of Fe layers across Cr interlayers. *Phys Rev Lett*, **57**, 2442; Baibich MN, Broto JM, Fert A, Nguyen Van Dau F, Petroff F, Eitenne P, Creuzet G, Friederich A & Chazelas J (1988). Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices. *Phys Rev Lett*, **61**, 2472.
15. Brus LE (1984), *J Chem Phys*, **80**, 4403; Efros AL & Rosen M (2000). *Ann Rev Sci*, **30**, 475; Cullity BD (1972). *Introduction to Magnetic Materials*. Addison-Wesley; Cullity BD (1978). *Elements of X-ray Diffraction*. Addison-Wesley Publishing Company, London.