



The Bonsai of Materials and Exploitation of its size dependent photoluminescence efficiency through ion irradiation

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Abstract

After a quick introduction of nanomaterials, the talk deals with the size-tuning of Nanoparticles by swift heavy ion irradiation and also deals with the benefit of ion irradiation expressed as increased efficiency of photoluminescence.

Key words : Nanomaterials, Ion Irradiation, Photoluminescence Efficiency.

Introduction

Here “The Bonsai of materials” is used to mean nano-materials. The prefix *nano* comes from the Greek word “nanos”. It means “dwarf”. These nanomaterials are thus materials at an extremely small scale, specifically within the range 1 to 100 nanometer. It is worth mentioning that a nanometer is one billionth of a meter. These Nanomaterials are thus a new class of materials between atoms / molecules and bulk material.

R.P. Feynmann, the Nobel laureate physicist outlined the idea of nano science and technology in a after dinner speech on December 29, 1959 (zyvex website) The title of the talk was “There is plenty of room at the bottom”.

Nanomaterials (Drexler, 1992; Ratner, 2008) exhibit interesting size- dependent electrical, optical and magnetic properties. This is because At the nanoscale, quantum mechanics comes into play at the nanoscale,. Because of quantum mechanics, nanoparticles behave differently as compared to bulk materials of the same stuff. Indeed the emerging properties in a rather small number of atoms are found to be different from the case when there are millions of atoms together in bulk matter. In fact, these properties are different from both atomic and bulk- level. For example, as the size decreases, bandgap of material increases. In condensed matter physics,

a band gap means an energy range in a solid where no electron states are allowed. states This bandgap controls electrical and optical properties. So through change in bandgap ,its electrical and optical properties can be controlled.

Also, because of compactness, there are splitting of energy levels in nanoparticles. So, even in magnetic applications, there is more control.

Metal nanoparticles (Ratner, 2008) are used for colouration. Further metal nanoparticles are much faster, in general, than semiconductor nanoparticles in switching. So these also have immense potentials.

Further because most of the particles reside in the surface, there is increase in surface to volume ratio of particles. This lead to increase in tensile strength, changes in melting point etc. So these effects can also be used to make new applications.

When all three dimensions of a piece of material is nano-scale, then the particular nano-material is referred to as quantum dot. Semiconductor quantum dots may be arranged in a matrix that has higher energy bandgap compared to the dot. Hence it can trap charge carriers.

Semiconductor quantum dots exhibit

1. Enhancement in the energy gap

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2. Discretization of the electronic levels
3. Large oscillator strength
4. High excitonic Bohr radius
5. Very high surface-to-volume ratio

These quantum dots may be created by (i) chemical method (ii) chemical vapour deposition method (iii) Lithographic methods and (iv) molecular beam epitaxy method.

To produce quantum dots chemically, colloidal chemistry is used. The process is analogous to producing an insoluble salt by precipitation from a mixture of soluble salts in solution. Here a stabiliser is used that prevents the precipitate from growing larger than nano-scale. Finally a capping layer is added to the dot thus prepared to stop degradation.

Characterization

Optical Absorption spectra of quantum dots of progressively smaller sizes exhibit blue shift of peaks as shown below. Accordingly, optical absorption study may be used as the first signature of nanoparticle fabrication.

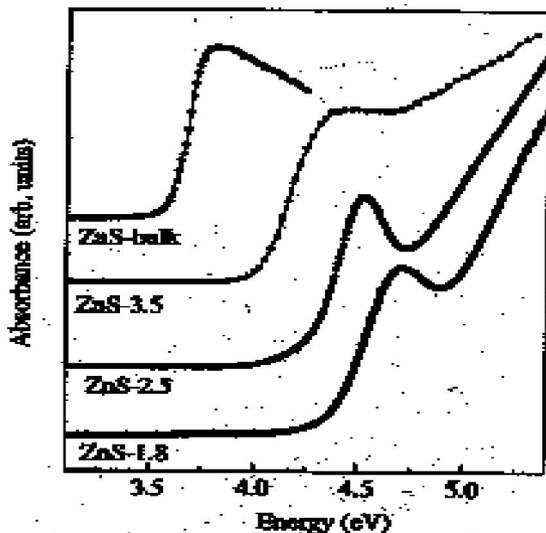


Fig. 1: Optical Absorption spectra of bulk material of ZnS and ZnS quantum dots of size 3.5nm, 2.5 nm and 1.8 nm showing blue shift

X- Ray Diffraction

It provides information on the average size of quantum dots in the sample. It also furnishes information on crystal structure.

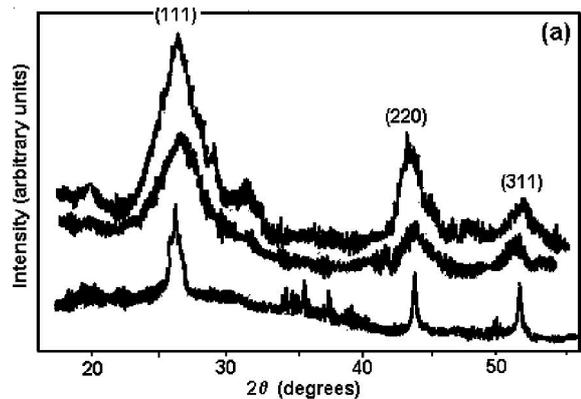


Fig.2 : XRD pattern of CdS quantum dots in (top) polyvinyl alcohol, (mid) styrene butadiene matrices corresponding to bulk CdS (bottom)

Transmission Electron Microscopy

Size of dots is further confirmed by Transmission electron Microscopy.

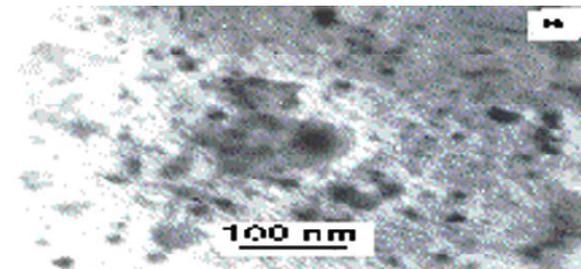


Fig. 3: Transmission microscopic images of CdS quantum dots in polyvinyl alcohol

In addition, Atomic Force Microscopy is used to study the surface topography of nanomaterials..

Size of quantum dots can be tuned to certain extent during synthesis to avail of its size dependent optical, electrical, magnetic and surface properties. Smaller the dot is, the shorter is the wavelength given out by it. The beam may be made more intense by tightly packing the dots.

Size Tuning with ion beam irradiation

Manganese doped zinc sulfide nanoparticles fabricated on polyvinyl alcohol matrix is

Bomarded with 100 Mev Chlorine ions. (Mohanta et al., 2003). The size of the crystallites is found to increase with ion fluence due to melting led grain growth under ion irradiation. The increased size as a result of grain growth has been observed both in the optical absorption spectra in terms of

redshift and in electron microscopic images. The photoluminescence (PL) study was carried out by band to band excitation ($\lambda_{ex} = 220 \text{ nm}$) upon ZnS : Mn, which results into two emission peaks corresponding to surface states and Mn²⁺ emission, respectively. The ion fluence for irradiation experiment so chosen were 1×10^{11} , 5×10^{11} , 5×10^{12} and 10^{13} Cl/cm^2 .

The irradiation was carried out on four identical samples. The nanoparticle samples were mounted on a vacuum shielded vertical sliding ladder having four rectangular faces. They were irradiated in the Mat. Sc. chamber under high vacuum (6×10^{-6} Torr) by using the 100 MeV Cl¹⁹ beam with approximate beam current of 170 pA (particle nanoampere), available from the 15UD tandem Pelletron Accelerator at NSC, New Delhi (Mehta and Patro 1988; Kanjilal *et al* 1993). The ion beam fluence was measured by integrating the ion charge on the sample ladder, which was insulated from the chamber. The fluence was varied in the range 10^{11} – 10^{13} ions/cm². In order to expose whole target area the beam was scanned over the x – y plane. The energy of the beam was chosen in such a way that the projectile range of the incident ion (as computed by SRIM program) exceeds

thickness of the sample films. Again, the ion beam energy and thickness of the target were selected so that modification due to electronic energy loss (S_e) affects the exposed sample. The nature of the ion beam induced modification has been analysed by using UV-VIS spectrophotometer in the range 200–800 nm and electron microscopy images. The photoluminescence spectra beyond band gap excitation show evolution of intense surface emission with fluence variations.

The energy of the beam was so selected so as to travel through the samples without stop. In otherwords, sample thickness (6.5 μm) was kept sufficiently lower than the projectile range i.e. 18.06 μm (table 1). As shown in the table for 100 MeV chlorine beam, electronic energy loss is predominant over nuclear energy loss and so we had to consider energy deposition due to the former cause. The electronic stopping power (S_e) of the beam was 553 eV/Å. The irradiation doses deposited in embedded Mn : ZnS/PVOH samples at four different fluences are calculated to be 0.539, 2.698, 26.98, and 53.95 joules, respectively. The amount of heat deposition as a function of fluence results into melting followed by grain growth (as illustrated in table 2)

Table 1 : Stopping energies and projectile range of energetic chlorine beam through ZnS : Mn/PVOH.

Energy (MeV)	Electronic energy loss, $S_e = (dE/dx)_e$ (eV/Å)	Nuclear energy loss, $S_n = (dE/dx)_n$ (eV/Å)	Projectile range, R (μm)
10^{-2}	11 \pm 19	63 \pm 32	1.702×10^{-2}
10^{-1}	33 \pm 02	58 \pm 21	7.782×10^{-2}
1	249 \pm 0	20 \pm 08	7.763×10^{-1}
10	502 \pm 5	3 \pm 92	3 \pm 30
100	553 \pm 0	0 \pm 58	18 \pm 07

Table 2 : Energy deposition with ion dose Energy deposition with ion dose and nanoparticle grain growth.

Irradiation dose (ions/cm ²)	Absorbed energy (Joules)	Absorption edge (nm)	Avg. grain size (nm)
0	0	310	11
1×10^{11}	0 \pm 539	314	14
5×10^{11}	2 \pm 698	320	18
5×10^{12}	26 \pm 976	325	32
1×10^{13}	53 \pm 952	326	41

This clearly shows that size varies with irradiation dose.

Swift heavy ion irradiation of the samples of bare and silica (SiO₂) coated ZnS quantum dots was carried out (S. Chowdhury et al 2008) with 160 MeV Ni¹²⁺ ion beam with fluences 10¹² to 10¹³ ions/cm². (Size enhancement of bare quantum dots after irradiation has been indicated in XRD and TEM analysis of the samples which has also been supported by optical absorption spectra. However similar investigations on irradiated coated quantum dots revealed little change in quantum dot size and emission.

SHI induced grain growth and grain fragmentation effects in polymer embedded CdS quantum dot systems have also been reported (Mohanta et al., 2004).

Thus irradiation can also be taken as a means of tuning the size of nanoparticle.

Higher pl efficiency by irradiation

The PL study is important as it provides information relating to different energy states available between valence band and conduction band responsible for radiative recombination. It has been found that the photoluminescent efficiency of coated ZnS : Mn nanocrystals is higher than the powder samples due to passivation of surfaces (Bhargava et al., 1994). The ZnS nanoparticles have a weak PL emission relative to Mn doped system. The band to band excitation in ZnS has been used to excite the Mn²⁺ emission. The subsequent transfer of electron and hole into the electronic level of the Mn ion leads to the characteristic emission of Mn²⁺ in ZnS (Brus 1986). In consistency with these reports, we have noticed yellow–orange emission for ZnS : Mn nanoclusters with peak wavelength ~ 582 nm. It is attributed to transitions involving d-electrons of the Mn²⁺ ions (Busse et al., 1976). The Mn²⁺ ion d-electron states act as efficient luminescent centres while interacting strongly with s–p electronic states of host ZnS nanocrystal into which external electronic excitation is normally directed. In an undoped quantum dot system, the external band edge as well as impurity related luminescent efficiency at room temperature is too low to be of any practical consequence. (Benisty et al., 1991). We also do not expect such emission

for undoped ZnS system (Fig. 4). With increase in ion dose, there is no significant shift of the emission peaks arising out of Mn²⁺. It is well known that when PL emission peak energies are less than the band gap energy of the material, these bands correspond to transitions involving donors, acceptors, free electrons and holes. The appearance of the PL peaks at energies substantially lower than the band gap suggests that transitions from energy states in the band gap are being favoured for the luminescence process in these nanocrystalline ZnS films (Pal, 1999). As depicted in figure 3, the first emission peak position shifts towards blue with increase in ion dose. We recognize these peaks as a result of trapped luminescence, which were reported in the form of broad bands in the PL spectra. Such peaks were attributed to the presence of surface states in nanocrystals. The surface emissions become more intensive with ion dose because the extent of free standing ZnS : Mn depends on degree of amorphization of the polymer matrix. The shift of surface emission due to size variation has already been discussed (Chestnoy et al., 1986). However, in case of second emission peak arising from Mn²⁺ site, particle size does not significantly affect the emission wavelength (Dinsmore et al 2000). In consistency with our observations, the shifting of surface emission peak towards blue is due to grain size.

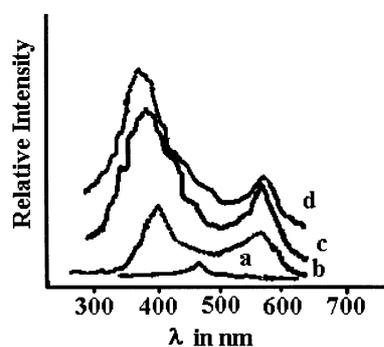


Fig. 4 : PL spectra of unirradiated a. polymer embedded undoped ZnS, and b. Mn doped ZnS, and ion irradiated c. 5×10^{11} ions/cm² and d. 5×10^{12} ions/cm² Mn doped ZnS nanoparticles.

The resulting intense emission may be suggested as net luminescence contributed by all the surface states, when the particles become fully free standing (for highest dose). Because for heavily dosed samples, the nanoparticles are supposed to be free from matrix encapsulation.

In conclusion, we claim that embedded polymer system is advantageous to observe regular grain growth process under ion irradiation. The size of the grains can be tuned by selecting proper ion fluence. The samples irradiated with highest dose are free standing and that is why strong surface emissions are visible in PL spectra which arise from the surface states. The surface emission

energy are calculated to be 3.179 eV, 3.236 eV and 3.296 eV for fluences 0.5×10^{11} and 5×10^{12} ions/cm², respectively. Moreover, the Mn+2 emission peak of irradiated samples does not shift appreciably but intensity improves because heavily exposed nanoparticles overcome barrier encapsulation.

However, surface emission shifts towards blue due to size effect. Therefore, sensitivity of the optical sensors supposed to be made of ion irradiated and doped semiconductors can be tuned by proper choice of ion dose.

In summary, ion irradiation can lead to both size tuning and higher PL efficiency.

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