LUMINESCENC PROPERTIES OF NANOMATERIALS

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Abstract

In recent times, engineering the structure and properties of nano-sized materials for numerous applications is getting tremendous attention. The term "nano" has been derived from the Greek words "Nanos" meaning dwarf or small size. Nano means 10-9 where 1 nanometer is equivalent to one thousandth of a micrometer or one millionth of a millimeter or one billionth of a meter. On reducing the size of particle from bulk to nano, physical and chemical properties (i.e. electronic, magnetic, catalytic, melting and optical etc.) are drastically modified compared to their bulk counterpart. Size of nanoparticles is intermediate between small molecule and bulk metal. There are different types of luminescence process on the basis of physical and chemical processes such as chemiluminescence, thermoluminescence, photoluminescence, mechanoluminescence and so on. There are lot of natural examples where one can see this process with naked eyes. Their excitation and emission position is definite and it is not influenced by quantum confinement effect, unlike semiconductors in which luminescence process is dependent on size dependent band gap. On the other hand, in organic based luminescent nanomaterials, it is a function of HOMO-LUMO conjugation length. Amongst rare earth elements, La3+ and Lu3+ do not show any luminescence which is attributed to either empty or completely filled 4f-orbitals.

*Keywords: Ionic Liquids, Optical absorption, photoluminescence, surfactants.*

Material and Methods: Ionic Liquids have been used as an alternative of organic solvents and surfactants. Ionic Liquids are the combination of cation and anion, that exist in liquid state in ambient conditions (at room temperature and in normal atmospheric pressure. Optical absorption spectroscopy and photoluminescence (PL) are used to understand the electronic transitions in the rare-earth doped nanoparticles. Time correlated single photon counting (TCSPC) was used to understand the relaxation dynamics of the rare-earth ion.

Luminescence Phenomenon in Nanomaterials: Nanomaterials have various physical and chemical properties and amongst them luminescence property is one of the most fascinating property. Luminescence is emission of light by substance. Sometime, it is also called cold body radiation emission. This process is attributed to chemical reaction, electrical energy, motion of sub-atomic particles and mechanical strain on the materials. There are different

types of luminescence process on the basis of physical and chemical processes such as chemiluminescence, thermoluminescence, photoluminescence, mechanoluminescence and so on. There are lot of natural examples where one can see this process with naked eyes. The most common example of luminescence is firefly which seems to glow at night. Besides, marine animals such as jelly fish, sea urchin, sea anemones, fungi, zooplanktons and phytoplanktons also show the luminescence process. This is also known as bioluminescence; which actually lies under the chemiluminescenc process, since, these luminescence processes occur due to the chemical reaction. For example in case of firefly, during the chemical reaction, luciferin molecules get oxidized in the presence of oxygen molecules, Mg_2+ and Luciferase enzyme by expensing of adenosine triphosphate (ATP), and then converted to Oxy-luciferin which shows luminescence.
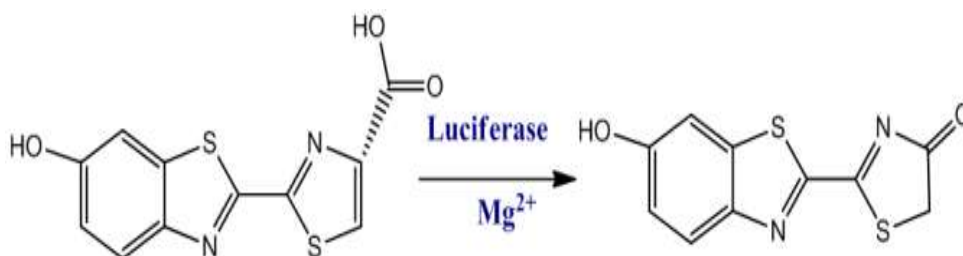
Luciferin Oxy-Luciferin

Some rare-earth ion doped (RE) and organic based luminescent nanomaterials materials possess luminescence process is fundamentally occurred due to electronic transition taken place from valance band (VB) to conduction band (CB), in different metastable states (MS) situated between the ground state (GS) and excited state (ES) and from highest occupied molecular orbitals (HOMO) to lowest unoccupied molecular orbitals (LUMO) in conjugated system of semiconducting, rare-earth doped nanomaterials and organic based luminescent materials respectively.Several factors that govern the luminescence property of nanomaterials will be discussed. In periodic table, there are seventeen elements such as scandium, yttrium, lanthanum and fourteen elements of lanthanide series i.e. from cerium to lutetium are known as rare-earth elements due to their less abundance in earth. These are commonly occurred in III (+3) oxidation state which can be generally represented as RE3+. Origin of luminescence centre in RE3+ is due to spin orbit coupling (2J+1) degenerate J-levels splitting, leading to generation of rich quantities of high electronic energy levels (excited state. However, extent of splitting is less than d-orbital splitting of transition metals. Number of allowed electronic energy levels can be calculated using the equation $14!/(14-n)!n!$, where n is the number of electrons in the *4f*-orbitals of RE3+ ions. These

intraconfigurational *f-f* electronic transitions are parity forbidden and well shielded by high energy filled *5s25p6* orbitals. As a result, there is no effect of external ligand field strength on the *f-f* electronic transitions. Thus, their excitation and emission position is definite and it is not influenced by quantum confinement effect, unlike semiconductors in which luminescence process is dependent on size dependent band gap. On the other hand, in organic based luminescent nanomaterials, it is a function of HOMO-LUMO conjugation length. Amongst RE elements, La3+ and Lu3+ do not show any luminescence which is attributed to either empty or completely filled *4f*-orbitals

Owing to doping of single or combination of RE ion/s, numerous luminescent centers are generated. As a result, several types of photodynamic process are taken place . For instances, singly doped rare-earth ion shows simple *f-f* electronic transition in which electron is directly excited from ground state to excited state. By non-radiative emission, it comes to lower level of excited state and then via radiative emission it relaxes to ground state. In addition of *f-f* transition, RE ions also show two other types of electronic transitions like *4f-5d* and charge transfer. *4f-5d* electronic transition is spin allowed and its emission intensity is very much susceptible to the external environment. While, charge-transfer transition such as ligand to metal charge transfer (LMCT) is obtained at higher energy (typically < 200 nm, except Eu3+, Yb3+ and sometime Sm3+ and Tm3+) compared to *f-f* electronic transition process. Thus, direct excitation is forbidden, and although being low absorption coefficient, less energy is required for exciting the RE ions than excitation via charge transfer process. In this way, luminescent feature of RE ions is notably dependent on excitation process.

The emission spectrum of Ce3+ is nicely overlapped with the absorption spectrum of Tb3+.Singly doped Ce3+ ions doped nanophosphors emit violet color. However, in Ce3+ and Tb3+ ions doped host matrix, on exciting the Ce3+ ions, energy transfer is occurred form Ce3+ ions to Tb3+ ions. Despite of violet color, now emission is occurred in green region of light which is emitted by Tb3+ ions. The extent of energy transfer can be determined using $\eta et = (1-Id/Ido) \times 100$; where ηet is energy transfer efficiency (%), Ido and Id is the luminescence emission intensity by donor in the absence and presence of acceptor. In this process, Ce3+ ions acts as energy donor and Tb3+ acts as energy acceptor. On the other hand, in downconversion process, high energy single photon is converted approximately to two low energy photons; for example Eu3+ ions doped with GdF3 and NaGdF4. Conversely, upconversion process which was independently illustrated by Auzel as well as Ovsyankin and Feofilov, in which low energy excitation photon is converted into high energy singly emitted

photon. This is attributed to presence of at least two real metastable states in between the ground and excited states. Upconversion process can be further divided into five categories: (a) excited state absorption (ESA), (b) energy transfer upconversion (ETU), (c) co-operative energy transfer upconversion (CET), (d) mediated photon-avalanche effect (PA) and (e) energy migration upconversion (EMU). In UC photodynamic processes, Yb^{3+} ions are commonly employed as sensitizer (S), however, Er^{3+}, Ho^{3+} and Tm^{3+} ions are doped as activators. Interestingly, Gd^{3+} ion is also incorporated along with Yb^{3+}, Tm^{3+} and other RE^{3+} ions ($RE^{3+}\sim Eu^{3+}$ and Tb^{3+}) in EMU process. In EMU process, on the basis of their response toward irradiated energy, dopant ions can be further classified as sensitizer (absorbing the energy, Yb^{3+}), accumulator (storing the energy, Tm^{3+}), migrator (transferring the energy, Gd^{3+}) and activator (emitting the absorbed energy, Eu^{3+}/Tb^{3+}).

Morphology of nanoparticles has also very significant impact on the luminescence property of RE doped nanoparticles, especially shape, aspect ratio and size of nanoparticles. Generally it is noticed that as the size of nanoparticles is reduced to certain range, surface defects increases leading to quenching of luminescence intensity. For illustrating the effect of morphology of nanoparticles on the luminescence intensity. Another important factor i.e. lattice strain which is also contributing significant role in tuning the emission intensity of RE^{3+} ion(s) doped host matrix, and can be calculated using the Williamson–Hall equation:

$$B \cos \theta / \lambda = 1/D + \eta \sin \theta / \lambda$$

On plotting the graph between $\beta \cos \theta / \lambda$ vs $\sin \theta / \lambda$, slope of the graph shows the lattice strain (η) and crystallite size (D) can be determined from the intercept. Positive and negative magnitude of slope indicates the tensile and compressive strain of the lattice strain respectively. Tensile strain is defined as deformation along a line segment that increases in length when a load is applied along that line, however in case of compressive strain this deformation decreases. Ghosh *et.al* illustrated how the changes in lattice strain of nanoparticles is taken place within various crystallite size and within tunable crystal phase of host materials.[75] For instances, it was noticed that nanorods of $LaPO_4$ doped with Yb and Er had higher tensile strain compared to the nanoparticles. On the other hand, compressive strain was observed for Yb coated $LaPO_4$ doped with Er nanorods and nanoparticles. In another example, same group further studied the Eu doped $LaPO_4$ nanocrystal and noticed that tensile and compressive strain were found for the hexagonal and monoclinic phase respectively. In addition, coated nanoparticles have shown compressive nature of strain than the uncoated and

rod shaped particles. It means lattice strain is significantly influenced by crystal phase, shape of host material as well as surface coating.

Afterwards, the synthesized RE3+ doped nanoparticles are used for different photonics and bio-photonic applications. For instances, to overcome the limitation (i.e. dimming and utilization of toxic elements like Hg) of conventional white light emitting sources such as compact fluorescent lamps (CFLs) and light emitting diodes (LEDs), now judiciously selected RE ions combinations are being incorporated into the host materials for getting energy efficient white light emitting materials. To achieve this, combination of blue, green and red light emitting or complimentary color emitting phosphors materials are used such as (1% Eu, 1% Tb, 1% Tm)-co-doped LaF3 nanoparticles and Dy3+ and Tm3+ doped phosphor material, β-NaYF4 nanorods doped with Yb3+-Ho3+-Tm3+ and by precisely doping Ce3+, Tb3+ and Eu3+/Sm3+ in suitable host materials may also generate white light.[79] Upconverting phosphors materials are recently incorporated with semiconductors for enhancing the solar cell efficiency. Large extent of loss of solar energy and band gap mismatch are major concerns in semiconductors and organic dyes based solar cell. Therefore, upconverting nanomaterials are incorporated with semiconductor based solar cell for enhancing the solar cell efficiency. It is assumed that using the upconverting phosphor materials, Shockley-Queisser efficiency may be enhanced up to ~40% from ~30%. For example, Shockley-Queisser efficiency of a 1.7 eV band gap solar cell is enhanced from 28.2% to 33.5– 43.6% by upconverting nanoparticles. NaYF4:Er3+ was employed for enhancing NIR silicon solar cell response. Further more, core-shell hexagonal NaYF4 :Yb3 +/Er3 + NaYF4, core-shell nanostructures of NaYF4:Yb3+/Er3+/Gd3+ nanorods which is coated with plasmonic Au nanoparticles or Au shells and hexagonal, core-double-shell structured β-NaYF4:Er,Yb2 SiO_2,TiO_2 are synthesized for enhancing the solar cell efficiency. On the other hand, for biological application like photodynamic therapy, sensing the biological species, in vitro-in vivo bio-imaging, nanoparticles must be either water soluble or dispersible. However, fluoride-based phosphor nanoparticles are generally less soluble and dispersible in water. Therefore, for increasing the solubility and dispersibility, RE3+ doped nanoparticles are first preliminarily functionalized with biocompatible organic molecules, silica and metallic nanoparticles etc. For instance, zinc phthalocyanine (ZnPc) (as photosensitizer) was used for modification of 50 nm-sized PEI (PEI = polyethylimine)/NaYF4:Yb3+, Er3+ nanoparticles which generate singlet oxygen upon exciting by 980 nm laser for killing the cancerous cells. Upconverting Er3+ doped NaYF4

nanoparticles and modified with gold nanoparticles can also be used for the detection of biological species by FRET-based bio-molecular sensing. Amino-functionalized β-NaYF4:Yb, Er UCNPs have been used as fluorescent probes in cell immunolabelling and imaging. Sub-20 nm sandwich-structured NaGdF4:Yb/Tm/NaLuF4:Yb/Tm/NaYF4 nanocrystals were fabricated for in vivo upconversion luminescence and computed tomography imaging. However, to incorporate the magnetic property in the nanomaterial, Fe_3O_4 nanoparticles were coated with NaLuF4:Yb3+,Er3+/Tm3+ to form nanocomposites having multipurpose applications like magnetic resonance, charge transfer and upconversion imaging.

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