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Luminescence property of nanoparticles and their use in plant imaging

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Abstract:

Photoluminescence is the emission of light, which persists after the excitation agency, is removed. The Luminescent materials are termed as phosphors. These phosphors generally consist of a host lattice and a luminescent center termed as an 'activator.' The activator ions are responsible for photoemission. The phosphors found widespread applications in various fields like Fluorescent lamps, LASERs, Paints, inks, up conversion material, White LEDs, in solar cells etc

Luminescent nanoparticles can be found in nature and can be synthesized artificially that has myriad applications in biology, medical field and agriculture. The synthesized luminescent nanoparticles have tuneable photoluminescence, good biocompatibility, low toxicity, good chemical and physical stability. There are emerging areas in plant development and research. In this article, the luminescence phenomena, its types, luminescent nanoparticles and their interaction with plant has been discussed.

Keywords: Luminescence, Photoluminescence, Luminescent nanoparticles, plant imaging.

1. Introduction:

Photo luminescence phenomenon is observed in nature and attracted humankind from ancient times since it is associated with colorful light emission. Our ancestors appreciated and wondered at light emission from the glowworms, certain glowing fungi and aurora borealis. Since then, many scientists are trying to give systematic explanation of this phenomenon. Major contribution to understand it was made by Zenchi in 1652 [[1]]. He described photoluminescence as the emission of light, which persists after the excitation agency, is removed (luminescence). Also, he proved that color of emission light is independent of excitation light and distinguished the phenomenon from scattering. About 200 years later, Stoke showed that the incident and emitted light differed in color and well-known Stoke's law was put forward [[2]]. In 1867, E.

Bequerel [3] distinguished two types of phosphorescence or after-glow, which were due to monomolecular and bimolecular decay mechanism.

In the recent years there are dramatic developments in the research on luminescence. There has been a phenomenal growth in the subject, and widespread applications are coming up. Luminescent materials are called as phosphors. The first systematic study of luminescent crystals was made by Lenard [4] and his school, at the beginning of the twentieth century. The phosphors they studied are called as 'Lenard Phosphors'. The practical applications of these phosphors in luminescent lamps, then accelerated this study further after 1930.

2. Luminescence Phenomenon

Luminescent system generally consists of a host lattice and a luminescent center termed as an 'activator' [5]. This activator absorbs the incoming excitation radiation and goes to the excited state. The excited state returns to the ground state through a quasi-stable state by emission of radiation leading to luminescence (Figure1). In some cases, the excitation radiation is absorbed by another ion termed as **'sensitizer'** which then transfer it to **[6]** the activator. In many cases the host lattice transfers its excitation energy to the activator, so that, the host lattice acts as the sensitizer.

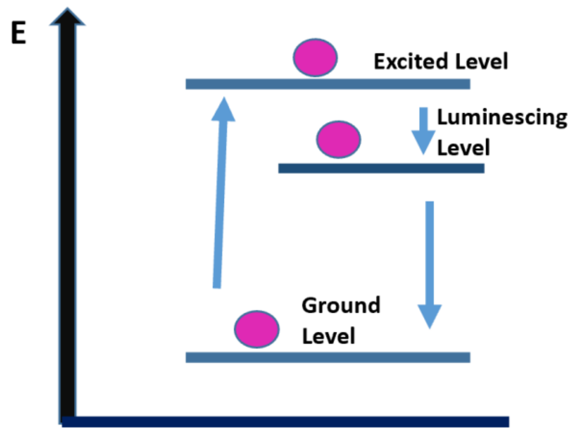

Figure 1: Luminescence Phenomenon

2.1 Excitation

In general luminescence may be excited by a number of agents such as light, cathode rays or positive ion bombardment or X-rays, by contact with flame, or by friction. The range and position of excitation band depends on host and the activator. The excitation band decides the practical application of the luminescent material.

2.2 Emission

The emission spectra of luminescent material may consist line or band emission or both depending upon the type of impurity. If the emission is in visible region of spectrum, the colourful emission can be observed. However, the phosphors with emission in UV region or in IR region are also useful for variety of applications in various fields.

3. Classification of luminescence

There are a variety of luminescence phenomena observed in the nature or in man-made materials. These can be classified on the basis of time lag or on the basis of excitation agency employed.

3.1 Classification of luminescence based on time lag

Luminescence is traditionally classified as fluorescence and phosphorescence. Phosphorescence named after the well-known optical property of element phosphorous [[7]]. In Greek the term 'phosphor' means 'light bearer'. According to modern conventions fluorescence refers to emission of relatively short persistence (10^{-6} – 10^{-12} seconds), whereas the phosphorescence persists considerably longer (sometimes even for seconds).

3.2 Classification of luminescence based on the type of excitation

Luminescence is classified depending upon the type of the excitation source [[8]]. A prefix added to the term luminescence usually indicates the excitation source. The classification of luminescence based on the source of excitation and their various applications [[9]] are given in Table 1.

Table 1: Types of luminescence and their various applications

Luminescence type	Excitation source	Applications
Photoluminescence	Photons	Fluorescent lamps, PL-LCD, Plasma display, LASERs, LSCs, Paints, inks, Up conversion material, White LEDs etc
Cathodoluminescence	Electrons	TV set, FED, Oscilloscope, Monitors, storage tubes, Flying spot scanners, Radars etc
Electroluminescence	Electric field	LEDs, EL displays, Diode lasers
Radio luminescence	Ionizing radiations such as X-rays or Gamma rays.	X-ray imaging, Scintillators, dosimeters etc
Lyoluminescence	Chemical reaction	Detectors, Analytical devices, Lyoluminescence dosimeters etc
Chemiluminescence	Chemical reaction	Analytical chemistry
Bioluminescence	Biochemical reaction	Analytical chemistry
Thermo luminescence*	Ionizing radiations	Radiation dosimeter, Archeological and geological dating, Forensic science etc.
Triboluminescence	Mechanical energy	Used in radiology, toxicology, pediatric cardiology etc.

Sonoluminescence	Ultrasound	Acts as a catalyst in many situations

4. Luminescent materials

In general, the luminescent materials i.e., phosphors are classified according to their application or according to the chemical forms. These include Inorganic materials (like Silicates [10], Borates [11]), Organic materials (like polymers or low molecular weight materials [12]) or Hybrid compounds (like organically modified silicates (ORMOSIL [13]))

4.1 Luminescent Centers

The preferred luminescent centers for synthetic materials are rare earth ions. In these ions, the electrons in 4f shell are screened by those in the outer shells (except for La^{3+} and Lu^{3+}) and as a result they give rise to number of discrete energy levels. Another popular type of luminescent center is Transition metal ions. These are an important class of dopants in luminescent materials as their emission colors are very abundant. Rare earth doped nanophosphor materials have potential to be used as bioimaging agents with some excellent properties [14]. They have good solubility in some polar solvents and are very stable in water for at least six months. When excited by NIR lasers they show excellent luminescence thereby showing the utility of these materials for biological imaging. In agriculture fields, the luminescent nanoparticles can have many applications such as controlled release of agrochemicals such as pesticides, fertilizers, and herbicides. This can revolutionize the agriculture field by increasing the crop production, nutrient value of the produce, creating resistance in plant against harsh environmental conditions and harmful diseases. In this aspect Phyto nanotechnology is the emerging area which studies the interaction of luminescent nanoparticles and plant responses, the use of nanoparticles in targeted drug delivery in plants and their adverse effect like entering these particles in the food chain [15]. These recent developments have opened wider avenues for the development of transgenic crops through the direct in situ delivery of various macromolecules, including genes and drugs, delivery systems, etc., smart agrochemicals, early detection of diseases and pathogens, plant protection chemicals and precise farming techniques [16]. However, this can only be done successfully in plants after increasing our knowledge about luminescent nanoparticles uptake, transport and accumulation in plants.

5 Plant imaging

Plant imaging can be a tool for visualizing structures of plant cells, which explain the signalling process on the membrane, not only revealing the formation of the overall plant tissue, but food transportation also can be studied. As compared to animal cells, imaging of plant cells with luminescent nanoparticles has not been reported much. It can be divided into two categories of plant imaging, in vitro Imaging and in vivo Imaging [Figure 2]. In vitro imaging comprises imaging of cell wall, cell membrane and organelles.

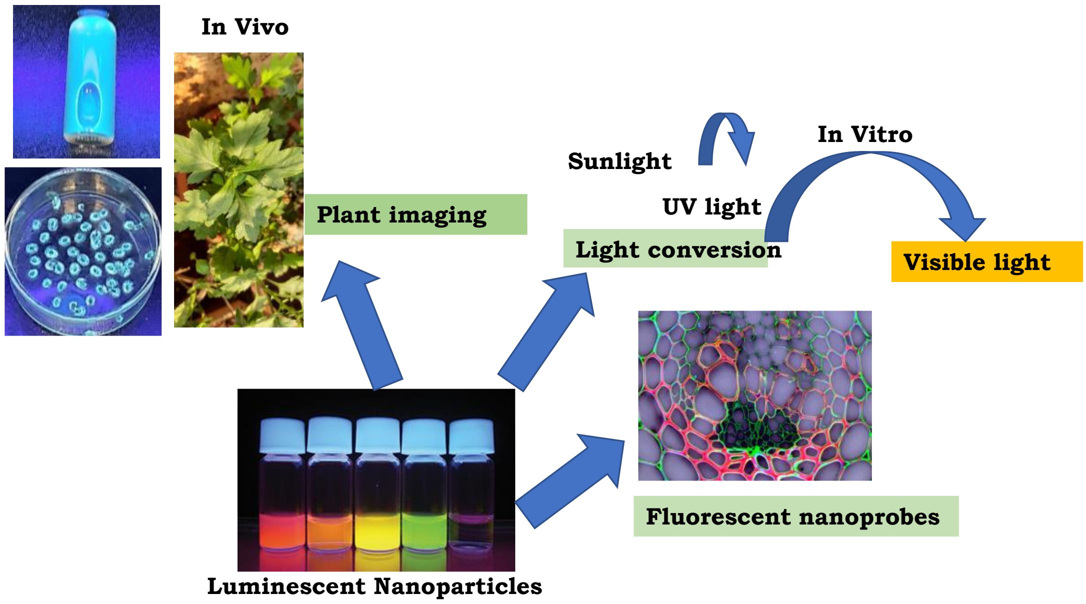

Figure 2: Applications of Luminescent nanoparticles

Multicolour imaging of cell walls was discussed using NaLuF4:Yb^{3+}, Er^{3+}showing green emission up conversion. This phosphor was modified by PEG so that it could disperse into cytoplasm while $NaLuF_4$:Yb^{3+}, Tm^{3+} nanophosphor showing blue emission are remained in the cell wall which are hydrophobic in nature [17]. Wang *et al* shows the controlled synthesis and multicolour emission of bifunctional $NaYbF_4$:Nd^{3+} @$NaYF_4$:Yb^{3+} active-core/active-shell colloidal nanoparticles for the possible application as a fluorescence and temperature nanoprobe [18]. The nature of cell walls, membrane and organelle are either hydrophobic or hydrophilic that can be used for multicolour imaging [19]. Using nanoparticle-borne imaging agents, we can also observe the movement of exogenous genes along the expression of transgenes by integrating these exogenous genes in a similar manner. Significant progress has been made in biology with the application of fluorescent QD bioconjugate [20].

6 Detection and Characterization of luminescent nanoparticles:

Research in plant technology will benefit from the development of better analytical methodology. Existing techniques (Table 2) can be divided into following techniques: (i) detection of extrinsic properties of nanoparticles in suspension or after acid/enzyme-mediated degradation plant tissue environment; and (ii) allow on-site analysis of nanoparticles in the plant.

Table 2: Analytical methods of nanoparticles

Sr No.	Techniques
1	Scanning electron microscopy (SEM)
2	Transmission electron microscopy(TEM)
3	Atomic force microscopy (AFM)
4	Dynamic light scattering (DLS)
5	X-Ray fluorescence microscopy (XRF)
6	X Ray Absorption Spectroscopy (XAS)
7	Ultraviolet- visible spectroscopy (UV-Vis)
8	Transmission X-Ray Microscopy (TXM)
9	Hyperspectral Microscopy
10	Fluorescence lifetime imaging microscopy (FLIM)

7 Conclusion and Future scope:

The new technologies related to interaction between plant and nanoparticles are still in their infancy, but they have the potential to produce firstly a new tool for the intelligent distribution of pesticides. And secondly a new method for delivering specific bioactive molecules for the manipulation and gene transfer of plant varieties. There is another approach which applies to imaging of plant cells. Unlike animal cells, in plants nanoparticles need to cross the cell wall before entering the cytoplasm. The interaction between nanomaterials and the cell wall is still poorly understood. Future research needs to focus on the generation of new nanoparticles that can expand or induce pores in the cell wall to facilitate the migration of nanoparticles through the cell wall and other barriers. Nanoparticle domains can be functionalized with biological identifiers and tags to enable specific targeted delivery. It has the potential to open up new ways of manipulating genes that are transiently or permanently expressed at the single cell or tissue level. Apart from this, the luminescent nanoparticles can be tuned to control the opening and closing of nanopores for drug load to enter in response to changing external conditions. This can be achieved by using pH sensitive nanofilms or ultrasound sensitive pore protectants. You can generate "smart" nanoparticles. Finally, it may be possible to design nanoparticles with nucleotides or activators capable of inducing plant defence in response to biological or abiotic stress. These advances in plant technology will create new opportunities for plant science and plant production systems.

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