International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 07 Issue: 04 | April - 2023 Impact Factor: 8.176 ISSN: 2582-3930

Design, Solution Synthesis, Characterization and Up conversion Studies of Phosphor

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Abstract: The inorganic nanomaterials known as upconverting nanoparticles (UCNPs) have the ability to transform low energy near-infrared (NIR) excitation light into visible and ultraviolet emission light. Due to the decreased light scattering, NIR light excitation reduces the autofluorescence background and permits deeper penetration into biological samples. UCNPs areattractive prospects for bioanalytical and biomedical applications due to their optical properties, however their performance is hindered by their poor optical brightness. Introduction, benefits of rare-earth-based upconversion phosphors, types of upconversion luminescence, applications of upconversion nanoparticles in bioimaging, motivation for the work, goal and purview of the work, and anticipated results of the proposed research work are all covered in this chapter.

1.1. Introduction

A special type of optical nanomaterials called upconversion nanoparticles (UCNPs) doped with lanthanide ions exhibits a wide range of electronic transitions in the 4f electron shell. These nanoparticles have the ability to upconvert two or more photons of lower energy into one photon of higher energy. The upconversion phosphors' distinct anti-Stokes optical feature has allowed for a variety of applications over the past ten years, including background-free biological sensing, light-triggered drug administration, solarenergy harvesting, and super-resolution microscopy [1-2]. Co-doping activator and sensitizer ions with closely matched intermediate-excited states is crucial to achieving high upconversion efficiency [3]. The upconversion efficiency of this doping process is strongly influenced by the separation distance between the dopants, and it calls for a rational design that enables ideal interactions of a network of the sensitizer and activator ions. In order to control the energy transfer process and, ultimately, the luminescence performance of the nanoparticles, it is necessary to manage the doping concentration in a specific nanoparticle properly [4] The fluorescent probes are crucial for identifying the target molecules and boosting the fluorescence signal in fluorescence bio-imaging [5]. As a result, the fluorescent probes utilised in this technique have a substantial impact on the effectiveness of fluorescence imaging of small animals. For in-vivo imaging, visible light excitation and near-infrared (NIR) light excitation offer a number of benefits, including deep penetration, modest auto-fluorescence, little

photobleaching, and low phototoxicity [6]. As a result, offering two photon-excited fluorescence imaging based on the anti-Stokes luminescence process turns out to be a helpful tactic for imaging the living brain and reducing auto-fluoroscence. These two-photon fluorescence probes, which need to absorb two coherent NIR photons almost simultaneously, have low two-photon absorption cross-sections, which are consistent with their relatively low two-photon emission efficiency [7]. Further, two-photon fluorescence imaging needs a pricey pulsed laser, often a femtosecond laser. Upconversion nano-phosphors (UCNPs), a new generation of luminous probes for bioimaging, have been proposed as an alternative. The literature review of the UC materials utilized in bioimaging is shown in Table 1 [8]. Fig. An NIR excitable upconversion phosphor's upconversion emission is shown in Figure 1.1.

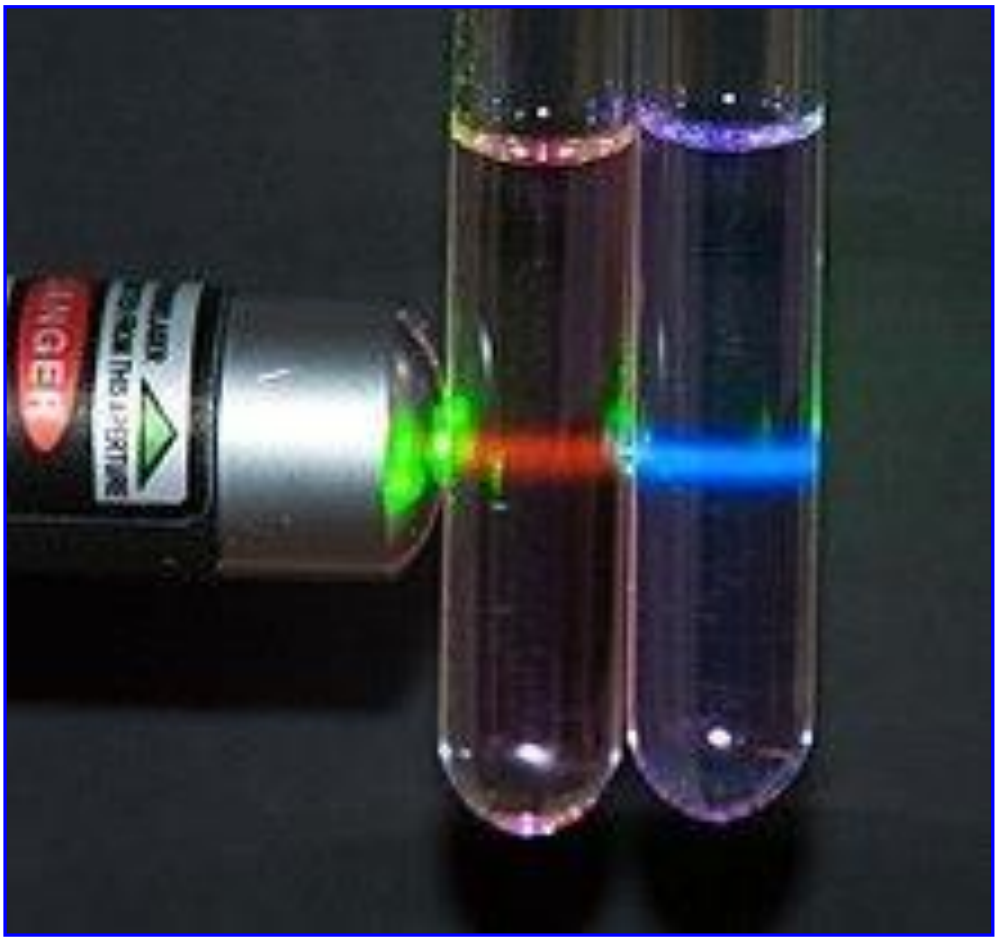

Fig. 1.1 Upconversion emissions of upconversion phosphors on NIR excitation

In the optical process known as upconversion luminescence (UCL), low-energy light—typically NIR light—is changed into high-energy light by absorbing several photons or transferring energy sequentially [9]. Since the middle of the

1960s, it has been thoroughly explored and is frequently used in optical equipment. For small animal bio-imaging, UCNPs have appealing properties: I infrared is less harmful to small animals; (ii) UCL-based Bio-imaging offers no auto-fluorescence from bio-samples because no bio-samples show UCL properties under CW excitation at 980 nm. In particular, lanthanide (Ln)-doping UCNPs exhibit unique UCL properties, such as sharp emission lines, long lifetimes. The use of UCNPs asprobes for the UCL emission of Tm^{3+} has been successfully demonstrated. The advantage with the technique is that even at great penetration depths, biological material can be visualised. UCNPs have so far been successfully used in small-animal imaging, including multimodal imaging, cell tracking, lymphatic imaging, and imaging of tumours.

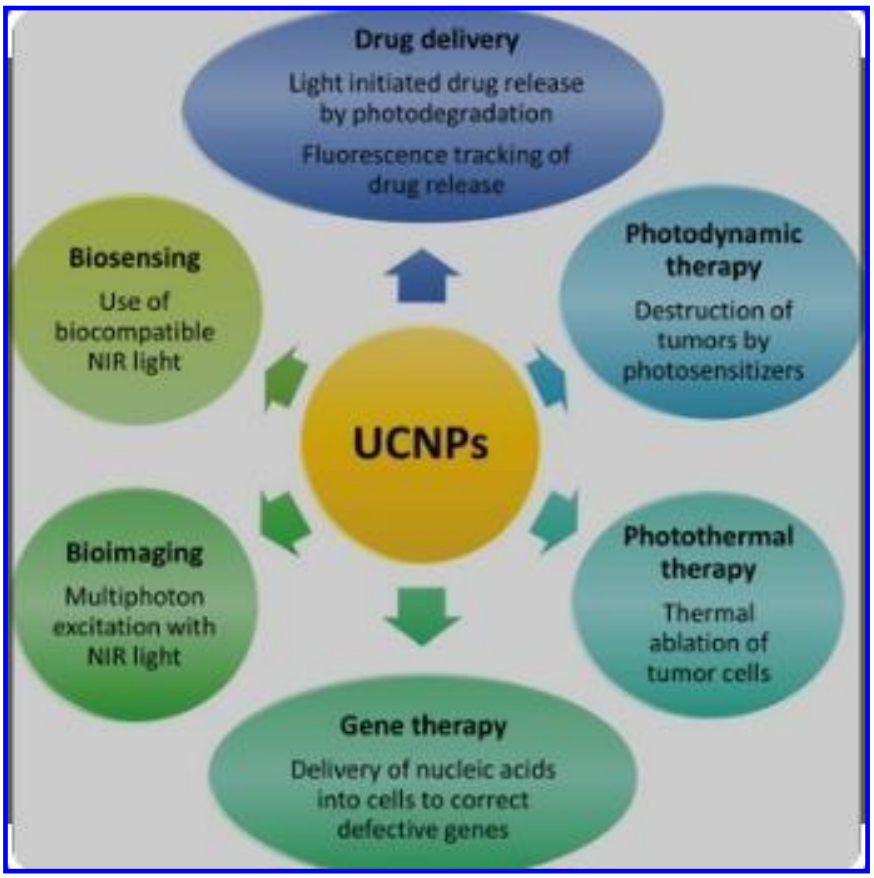

Fig. 1.2 Applications of upconversion nanoparticles

With the rapid advancement of nanotechnology over the past ten years, high-quality rare-earth doped

upconversion nanophosphors have been successfully manufactured and are becoming more common in biological sciences. A wide range of applications, including background-free biological sensing, light-triggered drug administration, solar energy harvesting, and super- resolution microscopy, have been made possible by this special anti-Stokes optical characteristic.Sensitizer ions must be co-doped with activator ions that have a closely matched intermediate- excited state in order to achieve high upconversion efficiency. The upconversion efficiency of this doping process is strongly influenced by the separation distance between the dopants, and it calls for a rational design that enables ideal interactions of a network of the sensitizer and activator ions. In order to maximise the energy transfer process and eventually the luminescence, a particular nanoparticle's doping concentration must be properly managed. Typical phase-based synthesis techniques include thermal decomposition, hydrothermal reaction, and ionic liquid- based synthesis.

Up-conversion nanoparticles and other nanomaterials are distinguished primarily by their ability to emit visible light when exposed to near-infrared radiation [9]. Low auto-fluorescence, decreased scattering and absorption, and deep penetration in biological samples are all effects of near infrared irradiation. The rational design and solution synthesis of upconversion nanophosphors doped with a variety of trivalent rare-earth ions, including Ho^{3+}, Yb^{3+}, and Er^{3+}, are described in this summary. For the production of the upconversion nanophosphors for bio- imaging, various synthesis approaches, including "Complex based precursor solution method," "Hydrothermal route," and "Template assisted method," will be used. One of the key constraints at the moment is the low luminescence efficiency of upconversion emission. As a result, selecting a suitable host material with reduced phonon energy is essential to achieving high upconversion luminescence efficiency (high phonon frequencies of the host lattice result in nonradioactive relaxation) [11,12].

1.2 Advantages of lanthanide-doped upconversion nanoparticles

Lanthanide-doped upconversion nanoparticles have provoked much attention due to their superior optical properties, which include high selectivity of emission, tunable color emission, long lifetime photoluminescence, large anti-Stokes shift, and narrow emission band [17]. UC nanomaterials now normally refer to lanthanide-doped phosphors in which lanthanide ions play the main role in the up conversion phenomenon [18]. Negligible auto-fluorescence background of this near infrared (NIR) excitation results in promising high signal-to-noise ratio for biological sensing and imaging studies. Second, the excitation wavelength is within the “biological window”, which is suitable for *in vivo*

applications due to the low photo-damage and high penetration depth [19, 20, 21, and 22], as displayed in Fig. 1.3. Third, these UCNPs are chemically stable and highly photo-stable with negligible photo bleaching and blinking. Also, good biocompatibility and ease of chemical fictionalization are also important for biological applications of photon up conversion using these UCNPs. This reflects the importance of the development of upconversion nanophosphor with high intensity.

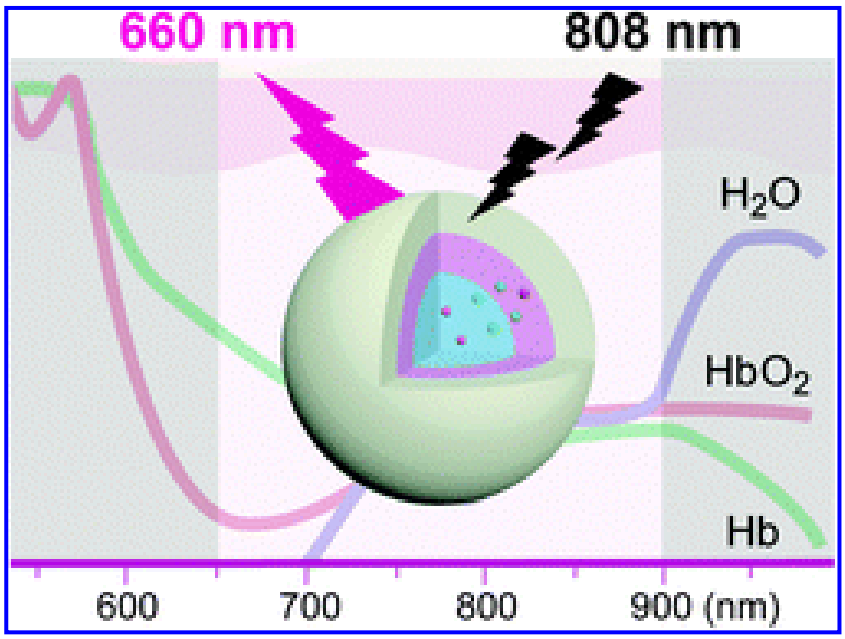

Fig. 1.3 An upconversion nanoprobe operating in the first biological window

1.3 Methods to enhance up-conversion efficiency

Although in theory very promising, the poor upconversion efficiency of the lanthanide-doped UCNPs restricts their use in practical applications. This multiphonon technique must typically beexcited by a high intensity laser, which makes it difficult to use in in vivo biological applications.To help with the design of UCNPs with improved upconversion efficiency, a number of chemical techniques are suggested. These include choosing the host and dopant, employing core- shell structure, and surface passivation. Low concentration dopants (often lanthanide ions) act as the matrix and luminous centres, respectively, in UCNPs, which are composed of a crystalline host. The host assists in positioning these luminous centres so that they

are more effective at up conversion (appropriate spatial distribution and ion-ion distance). Under NIR stimulation, the majority of host materials may emit visible light, but high up conversion efficiency necessitates strong coordination of the host lattice, dopant ions, and dopant concentration [23].

1.3.1 Choice of host

The host lattice's characteristics, which govern the spatial distribution and distance of dopants, coordination numbers, the kind of anions surrounding the dopant, and host-dopant interactions, have an impact on the upconversion process. For the selection of the host lattice, a number of variables, such as low phonon energy, low defects, and chemical stability, should be taken into account based on the mechanisms of up conversion. Low phonon energy in fluorides adds to their lengthy excited-state lifespan. Fluorides, on the other hand, frequently contain impurities that worsen multiphonon relaxation between the metastates, which significantly reduces the efficiency of their visible emission. While some heavy halogen ides exhibit reduced nonradiativeloss as well, they struggle with poor chemical stability. Metal oxides often have great chemical stability, however because of their high phonon energy, they have a low up conversion efficiency. One method employed to deal with this issue is the usage of core-shell architectures [24].

1.3.2 Dopant choice

As long as these states have comparable energy level spacing, UCNPs with long-lived excited states can consecutively absorb a second photon to higher energy states with a monochromatic light source. UCNPs commonly employ lanthanide ions with energy levels appropriate for this form of excitation, such as Er^{3+}, Tm^{3+}, and Ho^{3+}. The selection rules, however, disallow the 4*f*-4*f* transition, rendering this method incredibly ineffective. Increasing the concentration of dopants is one way to improve efficiency, but doing so comes at the tradeoff of a higher nonradiative deactivation rate and severe cross-relaxation. Practically, the doping level for Er^{3+} and Tm^{3+} cannot frequently surpass 3% and 0.5%, respectively. Light absorption in these UCNPs is still insufficient, even at the highest dopant concentration possible. Incorporating potent light-absorbing sensitizers is another method for ensuring enough energy transfer to the dopants. The most common sensitizer for Er^{3+}, Tm^{3+} and Ho^{3+} is codoped into the host lattice at high concentrations (18–20%). The matching of the energy level spacing between Yb^{3+} ($^2F_{5/2}$–$^2F_{7/2}$) and Er^{3+} ($^4I_{15/2}$–$^4I_{11/2}$ and $^4I_{11/2}$–$^4F_{7/2}$), allows for resonant energy transfer between the two ions, which is what gives rise to the sensitization ability [25].

1.4 Types Up-conversion Processes

For lanthanide-doped UCNPs, there are seven main up-conversion (UC) processes: excited state absorption (ESA), energy transfer up-conversion (ETU), photon avalanche (PA), cross relaxation (CR), cooperative activation up-conversion (CAU), cooperative sensitization up-conversion (CSU), and energy migration-mediated up-conversion (EMU). With the exception of the CR process, which typically lowers UC efficiency, all of these processes are nonlinear processes thatinclude absorption of several lower energy photons and emission of one higher energy photon (1). The long lifetime transition states of lanthanide ions in systems are responsible for this peculiar property.

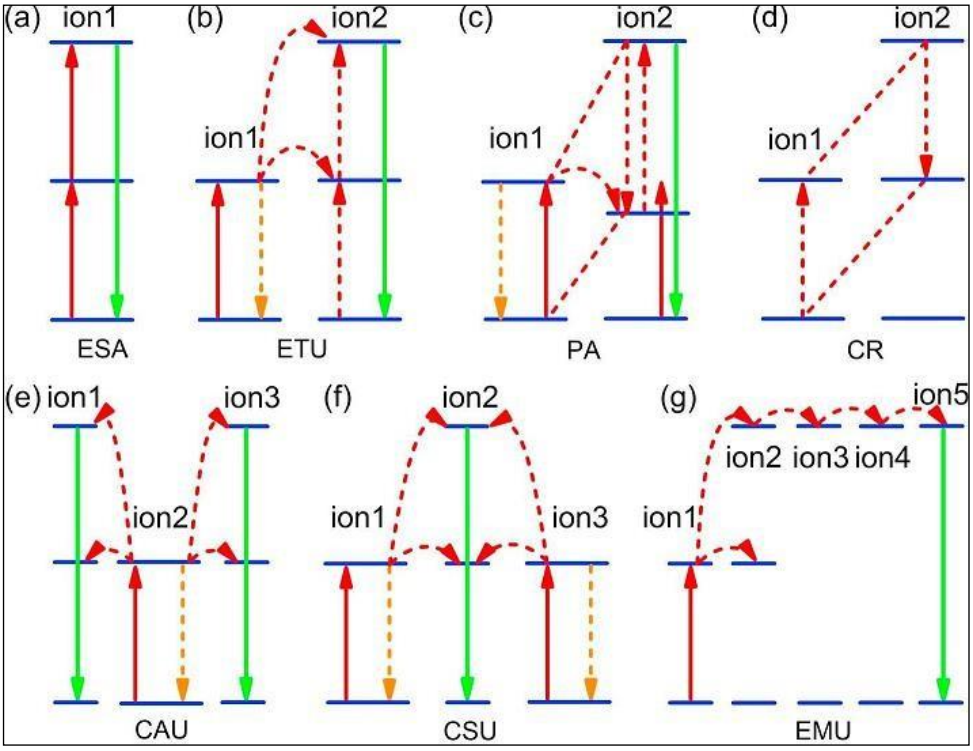

Fig.1.4 Schematic views of typical up-conversion processes lanthanide-doped UCNPs: (a) excited state absorption (ESA); (b) energy transfer up-conversion (ETU); (c) photon avalanche (PA); (d) cross relaxation (CR); (e) cooperative activation up- conversion (CAU); (f) cooperative sensitization up-conversion (CSU); (g) energy migration-mediated up-conversion (EMU). The red solid lines, red dotted lines, orange dotted lines andgreen lines represent photon absorption, energy transfer, spontaneous emission, and up- conversion emission, respectively. (For interpretation of the references to color in this figurelegend, the reader is referred to the web version of this article.)

As depicted in Fig.1.4 (a), ESA is a single-ion process that involves the sequential absorption of two or more photons and the emission of a photon with a higher energy. 1.4(a). Because Er^{3+} has a low cross section, this process often has low efficiency. In the ETU process, Fig. 1.4 (b), the majority of the pump photons are absorbed by nearby ions, which subsequently transfer energy nonradiatively to the emitters, which then release high-energy photons through excited state to ground state relaxation [26]. Fig. According to 1.3(c), the PA process uses an unusual looping mechanism that includes an effective CR and ESA for light excitation. This results in high up conversion emissions without any resonant ground-state absorption. As depicted in Fig., cross relaxation entails passing some of the first ion's excited energy to the second ion. 1.4 (d). The concentration quenching mechanism of emissions in CR is well established and significantly correlated with the dopant concentration [27]. With the exception of using it to adjust the colour output in UCNPs or build a productive photon avalanche mechanism, the CR process is typicallybest avoided when developing a UC system [28].

Three ions transmit energy through the CAU (1(e)) mechanism. In this instance, ion 1 and 3 are activators that release UC photons, whereas ion 2 is a sensitizer that, thanks to its high cross section, absorbs the majority of the low energy photons [29]. Ion 2 engages in simultaneous interactions with ions 1 and 3, collaboratively activating ions 1 and 3 through energy transfer. The excited ions 1 and 3 then release up-converted photons to return to their ground states. In a typical Er^{3+}, Tm^{3+} codoped system, the energy is transferred to Er3+ and Tm3+ concurrently by the Yb^{3+} (sensitizer) ions, which is followed by the emission of green/red and blue/infrared light from Er^{3+} and Tm^{3+}, respectively. The CSU process (Fig. 4(f)) is the opposite of the CAU process, with ions 1 and 3 typically acting as activators and ions 2 as sensitizers. Both ions 1 and 3 can be excited after absorbing excitation photons and transferring energy to ion 2, which can then be excited and release up-converted light. A core-shell structure and four lanthanide ions are used in Wang et al has suggested EMU process [8]. Through gadolinium sub lattice-mediated energy migration, efficient tunable up-conversion emissions in $NaGdF_4:Tm^{3+}/Yb^{3+}@NaGdF_4:Ln^{3+}$ (Ln^{3+}: Eu^{3+}, Tb^{3+}, Dy^{3+}, or Sm^{3+}) core shell nanoparticles were achieved in their design [30].

1.5 Upconversion Nanoparticles Used in Bioimaging

Because biological tissues and samples (including melanin, water, and haemoglobin) have a small window

of optical transparency for infrared photons, as shown in Fig. 1.5, UCNPs can be advantageous to existing biological imaging techniques. Due to their high emission penetration depth and controlled energy transfer capabilities, UCNPs have been developed as a novel family of fluorophores for biological applications [31]. Optical imaging is made easier due to the ability of infrared wavelengths to penetrate deep into tissue, but the light must be up converted in order to be easily detected by low-cost photodetectors. Furthermore, it enhances resolution and depth of field for bioimaging applications since the emitted visible radiation is not reabsorbed by fluorophores.

The absorption spectra of haemoglobin, melanin, and water—the three main tissue light absorbers are shown in Figure 1.5. Biological tissues can be easily observed using infrared radiation between the wavelengths of 800 and 1300 nm, which is known as the "optical window"of biological transparency. This window may be easily detected by modern optical detectors in bio-imaging applications thanks to the up-conversion absorbers, which can easily convert incident infrared light to visible radiation.

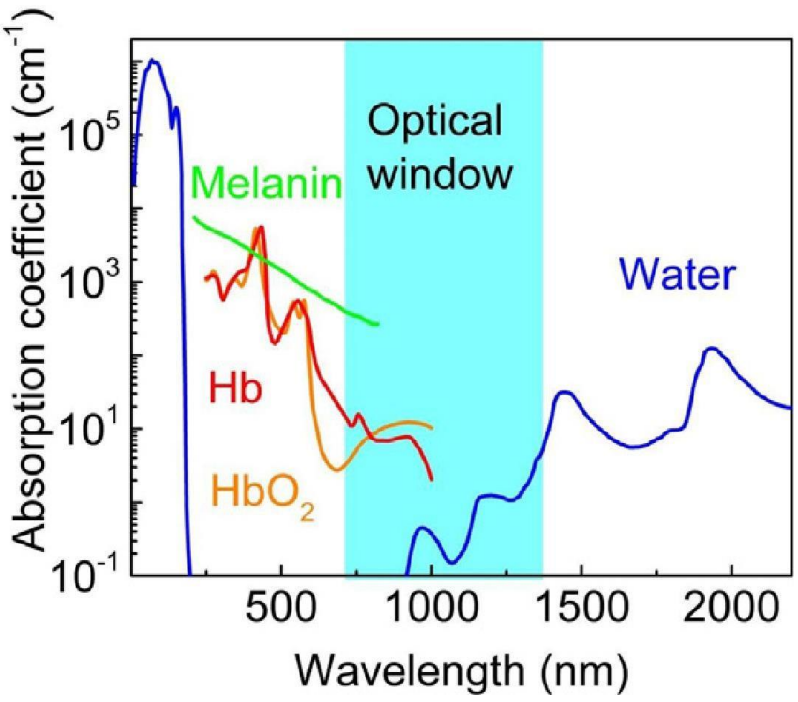

Fig.1.5. Absorption spectrum of hemoglobin, melanin and water

It is efficient to use stem cell therapy in conjunction with nanomaterials for regenerative medicine. Nanoparticles (NPs) can be delivered and precisely targeted to desired tissues or organs in addition to acting as therapeutic agent nanocarriers and scaffolds to guide the creation of new tissue. They can then be

employed in a number of imaging modalities for non-invasive real-time cell tracking and visualisation. NPs are comprised of a range of chemicals, including gold, iron oxide, cadmium selenide, and carbon, and have the potential to be used in regenerativemedicine.

However, there are still a lot of issues that need to be fixed, such as those related to toxicity, stability, and resident time. Important properties of upconversion NPs include their low toxicity, (ii) capacity to absorb light in an optical range where tissue absorption in tissues is least and penetration is greatest (it should be noted that they can also be designed to emit in the near- infrared range), and (iii) capacity to be used in multiplexing and multimodal imaging [32-45]. There is a review of the possibilities of upconversion materials in regenerative medicine. Regenerative medicine promotes the body's natural healing mechanisms to maintain, regenerate, and replace human cells, tissues, or organs that are harmed or no longer function correctly. Nanostructures can be important for implants or scaffolds for tissue engineering and cell therapy. As an illustration, surfaces can be nanopatterned to cause specific biological reactions in host tissue and organs [46–48].

As a result, the creation of new surfaces, structures, and materials containing nanoparticles (NPs) can provide the chance to mimic the environment in which cells naturally exist and to promote particular functions, such as cell mobility, cell adhesion, and cell differentiation, which would be directly related to the nanotopography of the biomaterial. The ability of nanomaterials to incorporate different functional elements into a single entity, or multifunctionality, is enabling significant advancements over current imaging, sensing, andstructural technologies. As a result, NPs are used in biomedical applications such as imaging (cell tracking and visualisation), therapy, drug delivery intended for target biological functions, surface modification of implantable materials, diagnosis, and even in the regulation of cell behaviour (adhesion, growth, and differentiation), which is crucial in regenerative medicine.

New intelligent biomaterials that can monitor and manage cellular regeneration might be implanted. For instance, NPs could enhance non-invasive regeneration therapies by keeping track on a disease (for example, through emission or magnetism) and promoting tissue recovery (e.g., through light-induced targeted administration). It's intriguing to note that stem cells have aninfinite ability for self-renewal; thus, research is focused on discovering strategies to recognise, draw, and mark these cells in order to monitor and/or initiate the regeneration process. Nanoparticles are also being researched as nanocarriers for theranostic applications.

With the aim of giving customised treatments based on in vivo molecular images to enable full

diagnosis, this developing field merges NP design with contemporaneous imaging and therapy, such as silica nanoparticles, carbon nanotubes, and gold nanoparticles (SNPs). Surprisingly, the prediction predicts that by 2020, at least half of all prescription drugs will be nanotechnology-based. Traditional non-invasive methods, such as positron emission tomography(PET) and magnetic resonance imaging (MRI), rely significantly on contrast chemicals and frequently don't have enough specificity or resident time to be a good choice for cell tracking. The majority of current approaches used to evaluate cell therapies entail invasive or harmful procedures, like tissue biopsies. Photonic applications in diagnostic, therapy, and interventional guidance are expanding. The limitations of biophotonic technologies for imaging often result from the light's shallow tissue penetration; however, for applications that rely on near-infrared (NIR) wavelengths and optical power (diffuse optics an) laser ablation of a desired target (irradiation density can provide spatiotemporal control and is simple to dose), localized imaging or laser ablation of a desired target can be carried out using fiber-optic based catheters (UCNPs can absorb two or more photons in the NIR range and emit at a higher energy level while still being transparent to visible light thanks to a non-linear conversion mechanism. Therefore, these bright NPs enable high-contrast optical biomedical imaging by lowering tissue auto-fluorescencein the backdrop and preventing considerable tissue absorption.

1.6 Motivation of the work

The synthesis and modification of UCNPs based on chemical matrix reactions have been documented along with their structure, energy levels, and various methodologies. Due to their distinctive characteristics, lanthanide-based UCNPs thrive in biological applications, including bioimaging and disease therapy. 1.6.

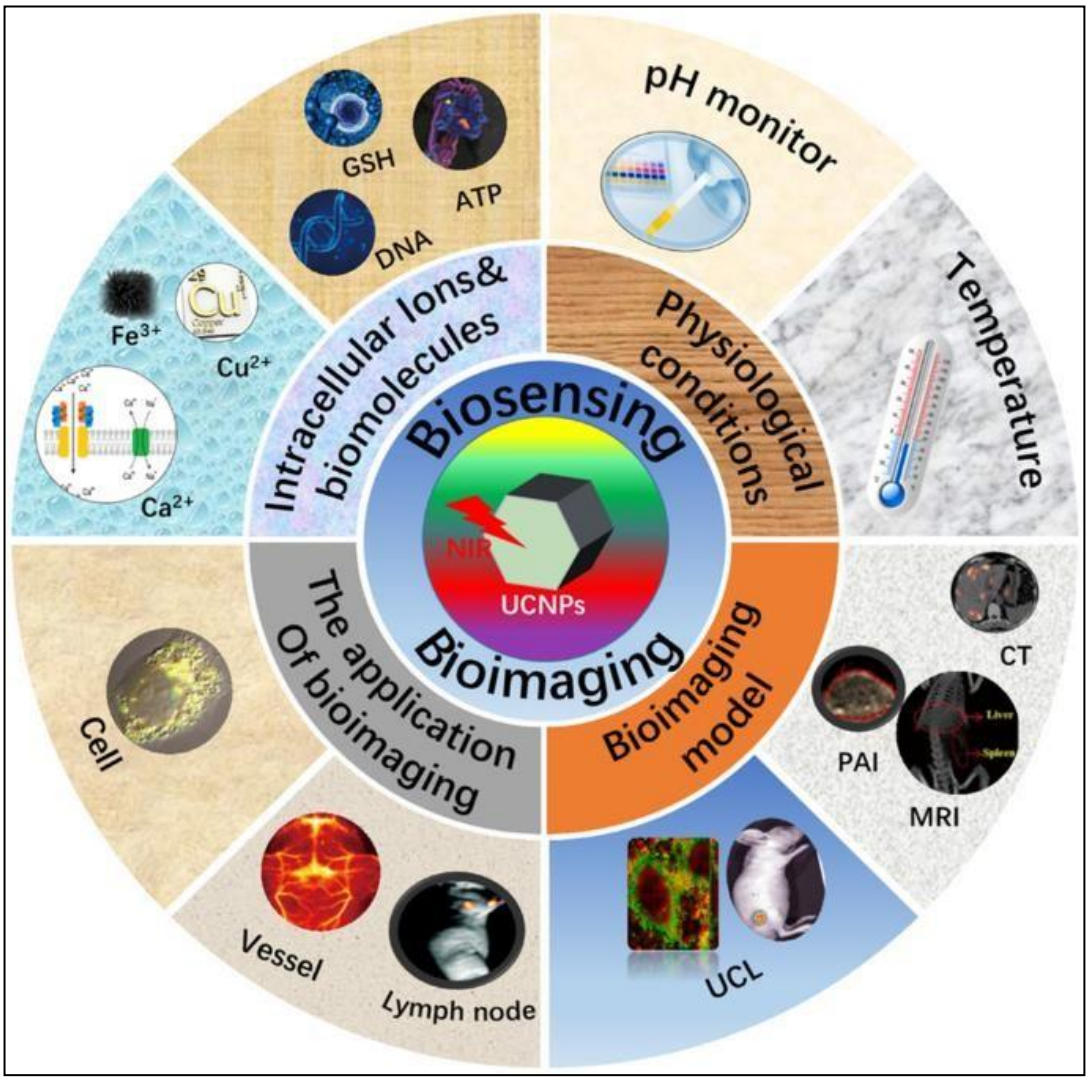

Fig. 1.6. Upconversion phosphor in Bioimaging and Biosensing

UCNPs showed promising clinical benefit and outperformed Photodynamic Therapy (PDT) for malignancies in terms of medication delivery and release. In addition, as illustrated in Fig. 1.6, the utilization of NIR light in UCNP-based PDT for antibacterial and biofilm removal applications represented a significant advance in the treatment of infectious diseases.

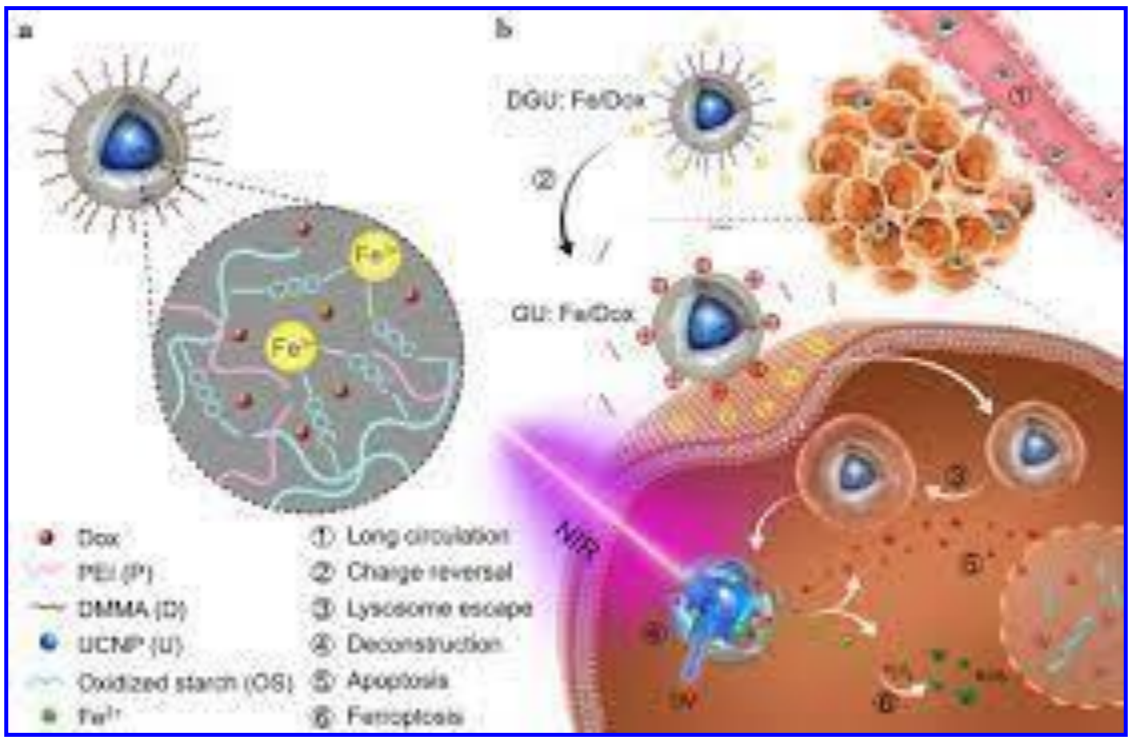

Fig. 1.7 Upconversion nanomaterials in bioimaging and disease treatment

The actual uses of UCNPs still must overcome significant obstacles, which will necessitate close collaboration between researchers from various fields. Although these luminous UCNPs have improved biosensing and bioimaging sensitivity and have photo-initiated chemical and biologicalreactions, their up-conversion efficiencies are still quite low, and much work has been put into increasing them. Using dye-sensitized UCNPs, the narrow-band NIR absorption can be broadened to a more useful wavelength range, however it was very unstable both in vivo and in vitro. To close the research gap in this field, it is possible to explore the synthesis of upconversion phosphor with improved upconversion efficiency by logically designing the host composition, dopants, and the synthesis process.

1.7 Objective(s) and Scope

Even though a number of quick and effective synthesis methods have been put forth for up- conversion material, there is still room for improvement in order to achieve precise control over the particle size, morphology, and distribution of phosphor particles that affect the luminescenceproperties for bio-imaging applications.

The present work deals with the exploration of the blueprint for the rational design, solution synthesis and characterization of rare-earth doped oxide based nano-phosphors by various feasible experimental techniques. The objectives of the present work are as follows:

- Rational design and solution syntheses of oxide based upconversion nanophosphors doped by several trivalent rare-earth ions such as Ho^{3+}, Yb^{3+}, Er^{3+}.
- Study of the structural, morphological and optical properties of the rare-earth doped as- synthesized nano-phosphors.
- Study of the effect of concentration of the rare-earth ions as dopant, on the structural and photoluminescence properties of the synthesized nano-phosphors.
- Investigation of the impact of the host composition such as YVO_4, Gd_2O_3 and Y_2O_3 on the luminescence properties of the as-synthesized upconversion nano-phosphors.
- Assessment of the effect of different synthesis methodologies like ‘Complex based precursor solution method’; ‘Co-precipitation technique’ as well as ‘Hydrothermal route’on the luminescence properties of the upconversion nano-phosphors.

1.8 An Overview of the Prior Research in This Area

Up-conversion nanophosphor development has received a lot of attention over the past few decades because of the wide range of intriguing applications they have, from optoelectronics to biological disciplines like drug delivery, biosensing, and cellular imaging. Table 1.1 provides a summary of some upconversion phosphor compounds and details on their hosts, dopants, excitation, and emission spectra.

Table 1.1 A schematic illustration of some upconversion phosphor researchpublished in the literature

Dopant	Host	Excitation (nm)	Emission (nm)	References
Er^{3+}	$NaYF_4$	1523	550, 660, 800, 980	31
Er^{3+}	CaF_2	1550	660, 980	32
Er^{3+}	$Gd_2(MoO_4)_3$	1530	545, 665, 800, 980	33
Er^{3+}	$NaGdF_4$	1530	527, 540, 653	34
Er^{3+}	Y_2O_3	1538	562, 659, 801, 987	35
Er^{3+}	Gd_2O_2S	1510	540, 660, 820, 990	36
Er^{3+}	BaY_2F_8	1557	540, 670, 800, 970	37
Yb^{3+}, Er^{3+} In^{3+}	$LiNbO_3$	1550, 980	530, 558, 672	38
Yb^{3+}, Er^{3+}	LaF_3	980	543, 655	39
Yb^{3+}, Er^{3+}	YF_3	980	525, 545, 656	31
Er^{3+}	Y_2O_3	980	560, 660	38

1.9 Expected outcome of the proposed research work:-

The expected outcome of this research work is the development of red and green emitting rare-earth doped upconversion nanophosphors for bioimaging. More elaborately,

i. Development of red emitting YVO_4:Ho^{3+}, Yb^{3+} upconversion nano-phosphors exhibitinghigh upconversion efficiency by complex based precursor solution method.

ii. Exploration of green emitting Gd_2O_3:Ho^{3+}, Yb^{3+} upconversion nano-phosphors by co-precipitation route.

iii. Synthesis of rod-like green emitting Y_2O_3:Er^{3+}, Yb^{3+} upconversion nano-phosphors byhydrothermal synthesis route.

iv.

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Chapter 2

Methodology

Abstract: Many techniques have been developed in recent years to synthesize phosphoric material. In the research methodology, we explain the methods that have been used for the synthesis of phosphorous materials that can be applied to the synthesis of up-converting and down-converting phosphorous materials. In this chapter, we have explained various synthetic routes, such as co-precipitation method, combustion method, sol-gel method, hydrothermal method, etc., which are used for thesynthesis of phosphoric material. We explain the synthesis methods such as the amorphous metal complex method, the combustion method and the complex base precursor solution method and the hydrothermal method, since these syntheses were used for the generation of the phosphoric materials studied in this work. . Search. Inthe present study, we have chosen the “complex-based precursor solution” route; "Co- precipitation technique" and "hydrothermal method" are used for up-conversion nanophosphorus synthesis.

2.1 Complex based precursor solution method

In the present study, we will apply a "complex-based precursor solution method using triethanolamine (TEA) as a complex agent" for the synthesis of YVO_4:Ho^{3+}, Yb^{3+} nano phosphorus by up conversion [1]. The manufacturing process involves the evaporation of aqueous precursor solutions consisting of stoichiometric amounts of the desired metalions complexed with TEA. TEA is an effective chelating agent that has good coordinationproperties with metal ions. Stoichiometrically, one to two moles of TEA per mole of total metal ions are required to form stable complexes with metal ions. However, the TEAmust be kept in the precursor solution in an amount greater than the required stoichiometric ratio. The reason for using the complexing agent, i. e.TEA in our synthesis procedure is its ability to form bonds with metal cations through its hydroxyl groups and nitrogen atom. TEA level must be properly maintained to control particle size.

2.1.1 Advantages of Complex Based Precursor solution Method using TEA

TEA is an effective chelating agent that has good coordination properties with metal ions[2].

1. Reduce processing temperature for synthesis, multipurpose.
2. Production of slightly agglomerated high purity particles.
3. Control of chemical homogeneity and stoichiometry.
4. Verification of the morphology of the TEA.
5. Cheap and readily available raw materials.
6. TEA is insensitive to moisture.

2.1.2 Mechanism of the Complexation Reaction

During the evaporation of the precursor solution, the TEA present in the system probably led to the formation of vinyl functions, which induce polymerization. As evidenced by FTIR investigation (Fig. 2.1(b)) of the resulting precursor solution, which was heated to 200 °C before decomposition. It presented a significant peak between 2900 and 3140 cm^{-1} due to polymerization due to the formation of vinyl groups during the thermal treatment of the precursor solution. But only the TEA without heat treatment showed no peaks as shown in Fig. 2.1(a) in the frequency range of 3000-3100 cm^{-1},confirming that the polymerization took place during the heat treatment of the complexes.

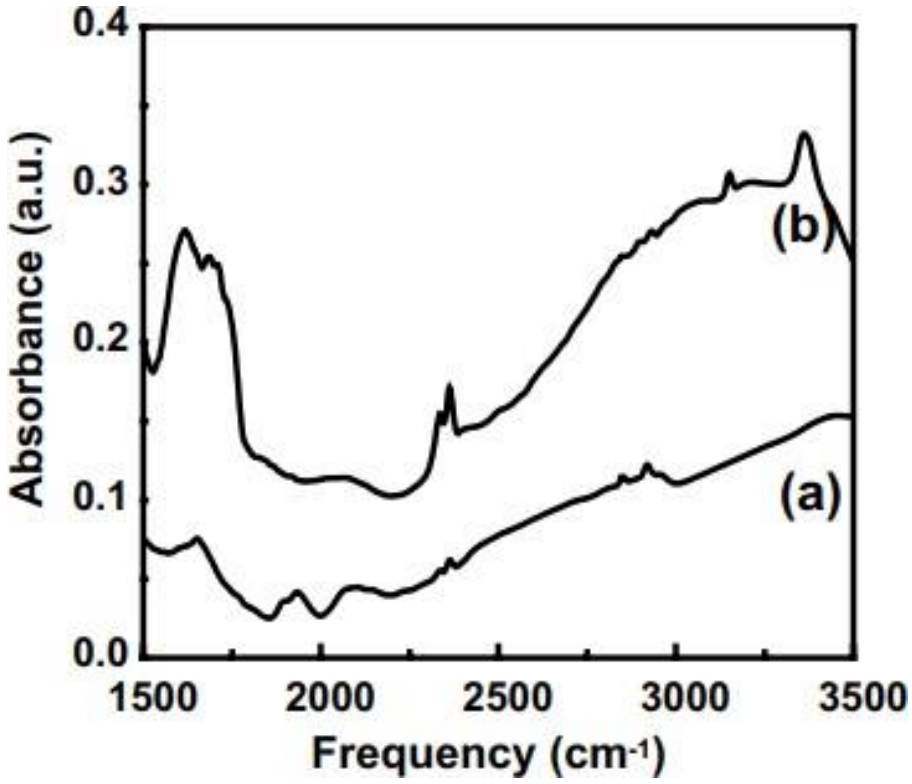

Fig. 2.1 FTIR of (a) TEA (triethanol amine) without heat treatment and (b) solution ofTEA complexed with metal ion just before decomposition.

2.1.3 Thermal Study

The DTA curves of FIG. 2 showed an exothermic thermal effect for all precursor materials with respective peaks between 380 and 500°C. The exothermic peak could be attributed to oxidation of carbon residues from decomposed metal complexes and TEA. The overall thermal effect was accompanied by the evolution of various gases (such as CO, CO_2, NH_3, water vapor, etc.), which was manifested by a single-step weight loss in the TG curves shown in Fig. 2. Above 500 ^oC, there was no significant thermal effect observed in the DTA curves and the corresponding TG curves did not show weight loss, which implies the complete volatilization of the carbonaceous compounds..

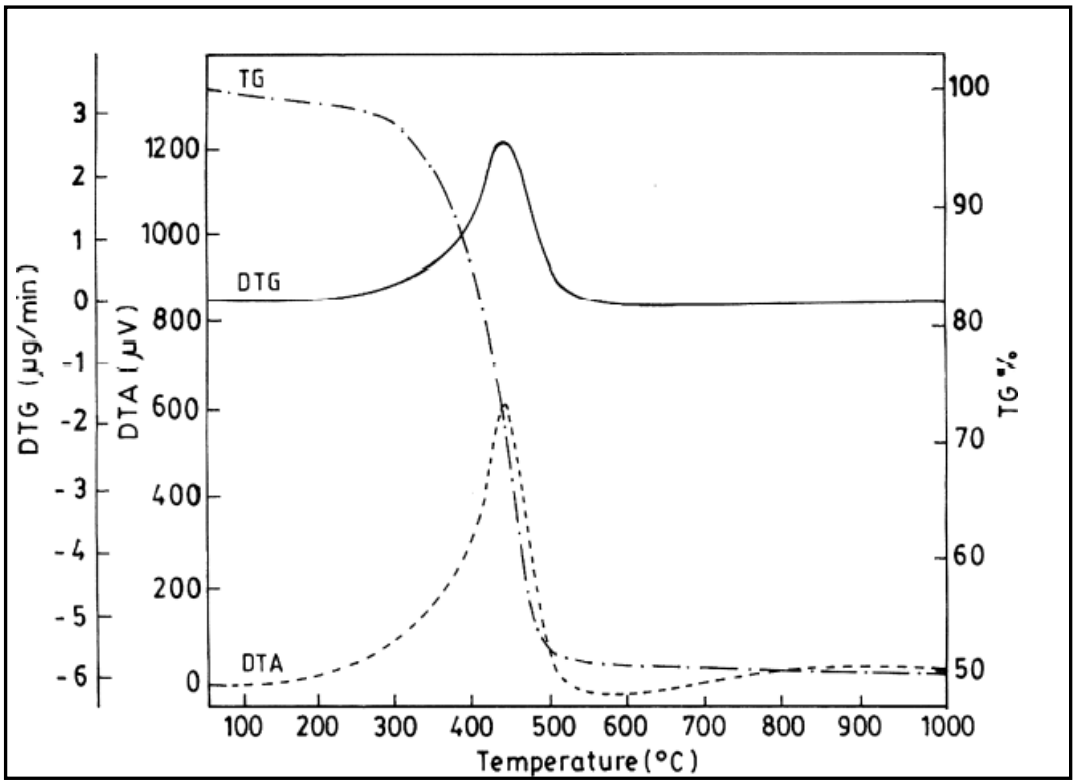

Fig. 2.2 simultaneously recorded DTA/TG of the precursor

2.2 Co-precipitation method

The required metal cations are co-precipitated in a common medium using the co- precipitation method,

usually as hydroxides, carbonates, oxalates, or citrates. In fact, the precipitating reagent is added to the solution after the corresponding metal oxides or carbonates have been digested with an acid. The final product is obtained by heating the precipitate formed after drying to the required temperature. The temperatures used in the ceramic approach are generally lower than the decomposition temperatures of the precipitates. Control of stoichiometry is difficult unless all metal ions form insoluble precipitates [3].

Co-precipitation (CPT), also known as co-precipitation, occurs when a precipitate carries with it chemicals that are generally soluble under the conditions used. Similarly, in medicine, co-precipitation refers to the particular precipitation of an unbound antigen and an antigen-antibody combination. In chemical analysis, co-precipitation is a key issue thatcan be both a drawback and a useful difficulty, as unwanted impurities often co- precipitate with the analyte, leading to additional mass in gravimetric analysis, where the analyte precipitates out. and its mass is measured. and used to determine its concentration or purity. purer particles) or dissolving the sample and re-precipitating it often solves this problem; On the other hand, co-precipitation is often the only method to separate an element in trace element analysis, as is often the case in radiochemistry. The traceelement is often co-precipitated using a carrier, a substance of comparable crystal structure that may contain the target element in dilute form (sometimes less than one part per billion) be precipitated by conventional methods. For example, francium can beseparated from other radioactive elements by co-precipitating it with calcium salts such ascesium perchlorate. The use of co-precipitation in radiochemistry dates back to Otto Hahn.

2.2.1 Advantages of Co-precipitation technique

1. High performance
2. High product purity
3. No need to use organic solvents
4. Easily reproducible
5. Low cost

2.3 Hydrothermal Method

Important subfields of inorganic synthesis include hydrothermal and solvo thermal synthesis. In addition to being widely employed in the fields of waste treatment and imitating geothermal and bio-hydrothermal processes, hydrothermal and solvo thermal techniques also take on a very broad definition that spans

numerous interdisciplinary scientific branches.

Hydrothermal synthesis, commonly known as the "hydrothermal process," is a special method for crystallizing compounds from hot aqueous solutions at high vapor pressures. Hydrothermal is a term with geological roots. A single crystal synthesis method that depends on the solubility of minerals in hot water under high pressure is known as hydrothermal synthesis. A device called an autoclave (see Figures 6.16 and 6.17) that contains a steel pressure vessel to which a nutrient is introduced in addition to water is used to develop crystals. There is a constant temperature difference between the growing chamber's two ends. The dissolved nutrient settles into a seed crystal at the cooler end while dissolving at the hotter end, causing the desired crystal to grow. The method is based on the observation that a lot of oxides can dissolve in an alkaline solution. The production of phosphorus has been the process's most effective application. The hydrothermal technique has the benefit of allowing for the re crystallization of the powder. It is also possible to regulate the grains' size and form. This approach takes a lot of time, though. A single crystal synthesis method that depends on the solubility of minerals in hot water under high pressure is known as hydrothermal synthesis. An autoclave, which is a steel pressure chamber where a nutrient and water are supplied, is where crystal formation occurs. The process is also exceptionally effective at producing massive, high-quality crystals while retaining strong compositional control. Theprocedure' drawbacks include the requirement for pricey autoclaves and the inability to watch the crystal grow [4].

2.3.1 Advantages of Hydrothermal Route

1. The ability to synthesize compounds of different morphology
2. The ability to synthesize large crystals of high quality

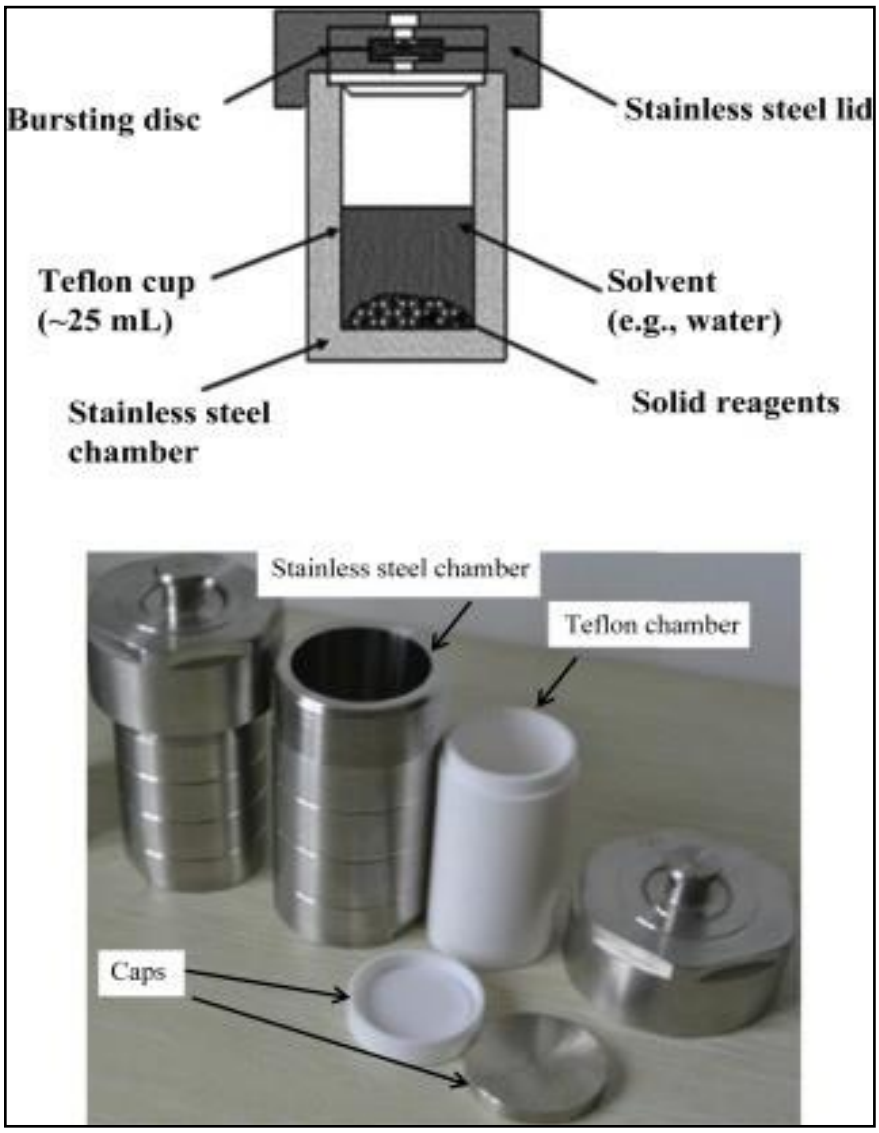

Fig. 2.3 Image of Teflon coated stainless steel autoclave

Hydrothermal autoclave reactors are those that carry out hydrothermal reaction processes but at high temperature and pressure. Two types of hydrothermal reactors have been developed, one is an autoclave with PPL tubes and the other is Teflon or PTFE. Both are coupled to each other by autoclave reactors.

Hydrothermal synthesis plays an extremely important role in the operation of autoclave reactors in order to carry out their applications in a more efficient and authentic way. Autoclaved hydrothermal reactors have become a success due to their specifications, adding value to these reactors and encouraging their use in our daily applications, promoting the prosperity of markets and industries at a higher level. The applications of this hydrothermal synthesis are numerous and validated, thus being able to increase the efficiency of

hydrothermal autoclave reactors and their generalization in today's world.

The hydrothermal reaction is carried out by using the reactor in a high temperature and high pressure hydrothermal autoclave. Generally, there are two types of hydrothermal synthesis reactors; The PPL line autoclaves are the first, while the second are hydrothermal autoclave reactors lined with Teflon or polytetrafluoroethylene (PTFE). Mainly two parts make up the hydrothermal reactor; Teflon or Teflon coated innerchamber and high quality stainless steel outer shell.