Frequency upconversion in catechin assisted LaF₃: Yb³⁺-Er³⁺ square nanoplates

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MS received 4 October 2017; revised 5 November 2017; accepted 6 November 2017; published online 25 November 2017

Abstract. Yb³⁺-Er³⁺ codoped lanthanum upconverting nanostructures with varying concentration of dopants have been synthesized by catechin method. The prepared upconverting nanostructures were characterized through XRD, TEM, XPS, NIR absorption, TGA and DSC analysis. TEM study confirms the formation of square-shaped nanoplates with size less than 100 nm. XPS peaks around 830–854 eV further reveal the formation of LaF₃ in the prepared samples. Frequency upconversion spectra from the developed nanostructures corresponding to the ²H_{11/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions upon 980 nm excitation are reported. Enhancement in the upconversion emission of catechin-based lanthanum nanostructures has been observed when compared with that prepared by ammonium di-n-octadecyldithiophosphate (AODTP) method.

Keywords. Upconversion; optical contrast agents; catechin; square nanoplates; hydrothermal synthesis.

1. Introduction

Lanthanides are better short wavelength luminescent host materials as well as dopants. Optical properties of the luminescent materials can be altered either by modifying the environment around rare earth ions or by incorporating the nanoparticles and/or by reducing the particle size.^{1–6} The uniqueness of the work stems from the fact that upconversion nanostructures (UCNs) have gained prominence due to their ability to overcome the known drawbacks such as auto-fluorescence from biological samples, high signal-to-background ratio, short penetration depth, etc., of down-conversion nanostructures (DCNs). In UCNs, the lanthanides have a special place because they can be easily excited under visible or near infrared (NIR) light due to their ladder like energy levels.⁷ The symmetry around the lanthanide ions also increases the efficiency of luminescence in the case of nanostructures, when compared to the bulk.⁸ Lanthanides-assisted upconversion lumines-

cence observed from inorganic matrices can be easily distinguished from organic complexes by its quantum yield and longer lifetimes.⁹ Upconversion emission can occur in one of the several ways such as, 1) ground-state absorption followed by excited-state absorption, 2) sequential energy transfer, 3) co-operative upconversion, 4) photon avalanche, and 5) combination of 1 and 3.^{10,11} Biocompatible UCNs have further advantageous applications such as in nucleotide detection, targeted cellular imaging, *in vivo* imaging, drug/gene delivery, photodynamic therapy, photo-induced drug delivery, sensing pH, gases like O₂, CO₂, heavy metal ions, screening, and immunoassays.^{12–14}

Inorganic fluoride-based host matrices *viz.*, NaYF₄, KYF₄, LaF₃, and LiREF₄ that can house the lanthanide ions to initiate upconversion luminescence have been reported.^{15–17} LaF₃ is considered as an ideal host matrix for luminescent lanthanide ions compared to that of the oxygen-based counterparts.^{18,19} The choice of fluoride

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hosts is justified by its low phonon energy ($\sim 350 \text{ cm}^{-1}$) which in turn prevents the nonradiative relaxations.^{20,21} Fluoride host also possesses low crystalline temperature, biocompatibility, photochemical stability and are transparent over a wide spectral window.^{22–24} The multi-site character of hosts provides active center occupancy for rare-earth ions in two or more nonequivalent crystallographic sites that possess low vibrational energy which minimizes the excited state quenching.^{25,26} Doping of fluoride hosts with optically active (Yb^{3+} and Er^{3+}) ions develops a robust fluorescence system.^{27–31} The key for a successful synthesis of LaF_3 nanoparticles through hydrothermal method lies in the judicious choice of the chelating (stabilizing) ligand.³⁰ The use of stabilizers in lanthanum fluoride synthesis can be explained in three points: 1) Acts as a phase controller for hexagonal phase; 2) controls the coordination between precursors in order to balance the nucleation and growth stage- for both morphology and size; and 3) Ligand capped nanostructures ensure enhanced solubility (water or organic solvents) as well as for bio-targeting applications. Usually, chelating ligands like EDTA, CTAB, citrate and catechin hydrate are employed. Unlike other ligands, catechin hydrate turns out to be a prominent ligand for its coordination on the surface of the nanostructures. Complete removal of unbound catechin as gaseous products without any carbon residues even at low temperature plays an important role.^{32,33} Further, surface coating with catechin plays a vital role in cell internalization pathway and also cellular entry through the plasma membrane.^{34–38} Though fluoride-based phosphors are well-studied for their luminescence properties,^{23,25,39} the choice of the template and the advantages that it could provide when one transits from synthesis to application creates scope for innovation. Here, the identification of the catechin – a natural polyphenol – as a template, is the main novel element. By doing so, a conventional coprecipitation is able to provide for a tuning of the luminescent properties. The template also replaces an otherwise not so favorable route of using AODTP due to its hydrophobic and toxic character for biological applications. This manuscript thus addresses the following: a) using a natural polyphenol – catechin – to bring about morphological changes to fluorides through a facile well established wet chemical synthesis route; b) providing a methodology to enhance the luminescent properties of the fluoride by way of using suitable activators.^{33,40}

Catechin-assisted synthesis of the Yb^{3+} - Er^{3+} codoped lanthanum-based nanostructures and their upconversion properties have been discussed in detail. This work also highlights a modulated synthesis where the

effect of dopant ions concentration and an annealing effect of the product at 600°C have been established.

2. Experimental

2.1 Materials and Methods

Catechin hydrate, Lanthanum (III) nitrate hexahydrate (p.a., $\geq 99.0\%$), Erbium (III) nitrate pentahydrate (99.9% trace metals basis), Ytterbium (III) nitrate pentahydrate (99.9% trace metals basis), Sodium fluoride (99.98% trace metals basis) were purchased from Sigma–Aldrich, USA and used without further purification. Ethanol was purchased from Hayman speciality products.

Phase and crystal structure of the prepared nanostructures were characterized by using a Rigaku Miniflex II desktop X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.540562 \text{ \AA}$). A scan rate of 1° min^{-1} in $10\text{--}80^\circ$ (2θ) range was employed. The operation voltage and current were maintained at 30 kV and 15 mA, respectively. Surface morphology of the prepared nanostructures has been collected using a Jeol/JEM-2100. The particle size of the prepared materials has been identified by using a Transmission Electron Microscope (TEM) operating at an accelerating voltage of 200 kV. The samples for these measurements were dispersed in ethanol under sonication in an ultrasonic pool for 30 min. UV-vis diffuse reflectance spectra (UV-Vis DRS) were recorded in the absorbance mode at room temperature in the range of 400–1200 nm by using Agilent Technologies (CARY-5000) double-beam spectrophotometer equipped with integrating sphere attachment using BaSO_4 as the reference. The sample is loaded onto the powder holder with a sphere diameter of 150 mm and sample size of $\sim 20 \text{ mm}$ (Figure 5). Thermal Analyzer TGA 1/1100 SF (METTLER TOLEDO) was used for Thermogravimetric Analysis (TGA) at a heating rate of 10°C/min under N_2 atmosphere. Q200, TA Instruments, Differential Scanning Calorimetry (DSC) was used at a heating rate of 10°C/min under N_2 atmosphere. X-ray Photoelectron Spectroscopic (XPS) analysis (Thermo Scientific, MULTI-LAB 2000, UK) was conducted to obtain the chemical bond information of the prepared samples. A Shirley background and Gaussian profiles were used to fit the experimental photoelectron peaks. The obtained binding energies (BEs) were calibrated with that of the carbon (C 1s) core level peak at 284.6 eV as a reference.

The upconversion (UC) emission spectra of the prepared nanostructures have been recorded in the range of 400–900 nm through a Princeton triple turret grating monochromator (Acton SP-2300) attached to a photomultiplier tube (PMT) upon excitation with 980 nm continuous wave (CW) diode laser at a fixed 615 mW power. The UC emission spectra of all the samples are recorded under the same experimental conditions. The position of the laser light relative to the samples was kept identical during all the measurements. CIE (Commission Internationale de L'Eclairage) colour coordinate analysis was carried by out using GoCIE software.

Table 1. Sample identifier and their corresponding dopants (Yb^{3+} and Er^{3+}) ions concentration for all the annealed Yb^{3+} - Er^{3+} co-doped La nanostructures.

Sample identifier	Yb^{3+} ion concentration (mol%)	Er^{3+} ion concentration (mol%)	Crystallite size (nm) ^a
F5Y2EA	5	2	50.4
F10Y2EA	10	2	73.1
F15Y2EA	15	2	47.0
F20Y2EA	20	2	42.9
F20Y1EA	20	1	48.2
F20Y3EA	20	3	51.7
F20Y5EA	20	5	83.5
F20Y10EA	20	10	67.6
CAT UCNs	14	3	31.0
AODTP UCNs	14	3	11.7

^aCrystalline size was determined from the powder XRD pattern according to Scherrer equation.

2.2 Preparation of upconverting Yb^{3+} - Er^{3+} co-doped lanthanum nanostructures

In the hydrothermal method, for the preparation of LaF_3 : 20 mol% and 10 mol% nanoparticles, 378 mg of NaF (9 mmol) was dissolved in 50 mL of double distilled water. Then 130 mg of catechin hydrate (0.45 mmol) in 50 mL of ethanol was added and heated to 75 °C for 30 min. To this reaction medium, a mixture of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.15 mmol), $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.23 mmol) and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.12 mmol) in 10 mL of water was injected slowly in drops which then resulted in brown precipitate immediately. After 2 h, the reaction mixture was placed in a hot air oven at 60 °C for overnight. The as-obtained product was washed thrice with anhydrous ethanol and water once by centrifugation (1500 rpm for 30 min). It was then dried in air to get the desired product, as a brown powder. Samples were annealed at 600 °C for 4 h and used for further characterization. The LaF_3 nanoparticles reported by AODTP method,⁴⁰ have been compared with catechin method for upconversion properties. The above procedure was repeated for a range of concentrations and tabulated in Table 1.

3. Results and Discussion

La based nanostructures co-doped with different amounts of Yb^{3+} and Er^{3+} ions have been synthesized. The exact doping level and the respective sample identifier with their crystallite size are given in Table 1. The powder XRD patterns for all the samples are provided in the supporting information. All the samples were crystallized with the solid mixtures of LaF_3 (Hexagonal JCPDS-10-721435, Space group: P6322 (182)),⁴¹ La_2O_3 (Hexagonal JCPDS-5-0602, Space group: P-3 mL(164))⁴² and LaOF (Trigonal JCPDS- 6-0281, Space group: R(0)).⁴³ A significant observation from the XRD measurements is that highly crystalline products (indicated as sharp diffraction peaks) can be obtained at a low reaction temperature (75 °C), short duration (2 h)

of hydrothermal treatment and catechin molar ratio of 0.05 with that of lanthanum. This observation could be attributed to the low solubility of fluoride that leads to easy precipitation. The XRD patterns of all the prepared samples before and after annealing is shown in Figures S1 and S2. The peak positions of the UCNs before and after activation at 600 °C for 4 h remains constant with some changes in the XRD peak intensity. The XRD patterns of **F5Y2EA** nanostructures with low dopant concentration (Yb^{3+} , Er^{3+} = 5 mol%, 2 mol%), before and after annealing treatment has to be singled out (Figure 1). The XRD pattern of F5Y2EA has been unexpectedly indexed to a mixture of hexagonal LaF_3 , La_2O_3 and trigonal LaOF phases. This could be attributed due to the oxygen contamination in the formed product. This is further confirmed from the TGA analysis as well as the temperature dependent heat flow for annealed F5Y2EA sample as shown in Figure 2. F5Y2EA are relatively stable and show a slight total weight loss of about 7%, possibly due to vaporization of physically adsorbed water and oxygen related impurity. The weight loss of 2.8% in the range RT to 125 °C, corresponds to the bound water molecules on the surface of the nanostructures, which is further confirmed by endotherms at around 100 °C and 120 °C. The second part, with a total weightloss of about 1.4% in the range 125–640 °C, corresponds to the loss of water molecules and is further confirmed by an endotherm at about 240 °C. The presence of water molecules can be explained by the partial hydration of LaF_3 leading to $\text{LaF}_3 \cdot x\text{H}_2\text{O}$, where $x \leq 0.5$. The presence of hydrated compounds is detrimental to applications like optics, and it is therefore necessary to provide an annealing treatment to ensure completely dry condition.^{19,44} LaF_3 is very reactive to oxygen impurities and then leads to La_2O_3 . The formation of lanthanum oxyfluoride could be possible due to the diffusion of oxygen and high mobility fluorine

Figure 1. XRD patterns of F5Y2E. (a), (b) represents annealed and as-prepared Yb³⁺-Er³⁺ co-doped LaUCNs respectively. Standard LaF₃, La₂O₃, LaOF corresponds to JCPDS 10-724135, JCPDS 05-0602 and JCPDS 10-895168, respectively.

vacancies in the lattice.^{45–48} The crystallite size of the annealed UCNs was calculated according to the Scherrer equation (Table 1). Irrespective of the dopant (Yb³⁺ and Er³⁺) concentration, the XRD crystallite size was found to be in the range of 31–83 nm.

It is predicted that the whole chemical reaction proceeds as follows:

It seems that heating irradiation (60 °C for overnight) induces the generation of oxygen contaminants, which in turn produces other lanthanum compounds.

In this method, Catechin (Biocompatible polyphenol) was employed as chelating ligand for the synthesis of lanthanum fluoride with different morphology in

Figure 2. TGA (a) and DSC (b) analysis of F5Y2EA.

hydrophilic nature for biological applications. The addition of lanthanum nitrate to sodium fluoride results in a chemical reaction between the La³⁺ cation and the F⁻ anion, resulting in the formation of LaF₃ nucleates and thus the nanostructures. This has been ascertained from TEM micrographs. The TEM micrographs of synthesized La nanostructures with high ytterbium concentration (20 mol%, F20Y1EA) and low ytterbium concentration (5 mol%, F5Y2EA) with erbium concentration of 1 and 2 mol% respectively are shown in Figure 3. The nanostructures in Figure 3a can be seen to consist of homogeneous small particles with an average size of 9 ± 2 nm. These smaller particles cluster in an oval fashion leading to larger agglomerates. F5Y2EA consists of irregular square nanoplates with mean length and diameter of 50 ± 16 nm and 48 ± 17 nm, respectively. Formation of irregular 2D square nanoplates is attributed to the adsorption of anions in the reaction system on the (0001) facets of the crystal seed and thus suppressing the crystal growth.⁴⁹ Annealing could result in clustering of nanostructures, as can be observed from the difference in size measured from both TEM and XRD. The corresponding SAED pattern demonstrates the polycrystalline nature (LaF₃, La₂O₃ and LaOF). In addition, the specific interaction of LaF₃ crystal facets with catechin conformers (A and E) leads to the morphological change.³³

In order to shed more lights on the distinctive information of elements indicating chemistry, composition and electronic properties in F5Y2EA, XPS analysis has been carried out. XPS spectra of La 3d, F 1s, and O 1s core level for annealed and as-prepared F5Y2EA are shown in Figure 4. The La 3d XPS spectra are fitted as a superposition of four Gaussian components. The two main peaks at 834 eV and 851 eV can be ascribed to two spin

Figure 3. Representative TEM micrographs (Inset as SAED pattern) and their corresponding particle size distributions of F20Y1EA (a, c) and F5Y2EA (b, d, e) nanostructures.

orbits of $\text{La } 3d_{5/2}$ and $\text{La } 3d_{3/2}$ respectively.⁵⁰ The other two peaks observed at 837 eV and 854 eV correspond to $\text{La } 3d$ satellite peaks.⁵¹ The doublet peak of each spin-orbit splitting reflects states with $[3d^9]_{\text{hole}} 4f^0$ and $[3d^9]_{\text{hole}} 4f^1$.⁴⁵ As a result of $4f^0$ and $4f^1$ mixing, $4f^0$ dominates low binding energy signals, and high binding energy is correlated to $4f^1$ peaks. $\text{La } 3d_{5/2}$ and $\text{La } 3d_{3/2}$ peak shifts to 843.63 eV and 860.44 eV, and satellite peaks shift to 847.57 and 864.98 eV for without annealing samples.⁵² The $f^1 - f^0$ separation values are 3.94 eV and 4.54 eV for as-prepared sample and 3.1 eV and 2.73 eV for annealed samples, as $f^1 - f^0$ values reflect different contents of La in lattice sites, as reported for La-doped ZnO .⁵³ The $\text{La } 3d_{5/2}$ and $\text{La } 3d_{3/2}$ splitting distances for annealed and as-prepared samples are estimated to be 16.99 eV and 16.81 eV respectively, which further confirms the occupancy site variation of La with respect to annealing.

The formation of LaF_3 is very well revealed by F 1s peak at 684.1 eV in association with $\text{La } 3d$ peaks. The two structures, the main one at 693.25 eV (684.10 eV) and satellite peak at 684.56 eV (674.60 eV) are represented for as-prepared (annealed) samples. It also clearly indicates the presence of lanthanum oxyfluoride

in addition to the observations during XRD measurements. Formation of lanthanum oxyfluoride can be well-understood from the oxygen XPS spectra.

The O 1s spectra consist of two components with binding energies at 540.51 eV (530.15 eV), and 532.31 eV (520.43 eV) corresponding to as-prepared and annealed samples. Before annealing, the shift of 10 eV to higher binding energy has been observed and due to the encapsulation of catechin on the surface of UCNs. The intensity of two components is strongly affected by the annealing process. These two component structure ($\text{O}_1\text{-O}_2$) is associated to the oxygen ions O^{2-} in (La_2O_3 and oxygen ions in LaOF). This can be explained that mobile F ions in LaF_3 migrate through the lattice, form volatile species and thus leave the system. This causes the oxygen contaminants in the reaction system with newly formed La phase and fluorine deficient La fluoride to form La_2O_3 (O_1) and LaOF (O_2).^{46-48,54} The full width at half maximum (FWHM) for these two contributions was observed to be 2.4 eV. The intensity of O_1 component is relatively higher than that of the O_2 component and this can be correlated to a higher proportion of La_2O_3 when compared to that of LaOF . Thus, the

Figure 4. XPS curves of the La 3d, F 1s and O 1s region for the annealed (a) and (b) as-prepared F5Y2EA UCNs.

splitting clearly shows the different chemical bonding nature of the corresponding atoms.

To evaluate the prepared nanostructures as upconverting nanostructures, different concentration of dopants

Figure 5. Absorption spectra of annealed F5Y2EA UCNs. Sample preparation details are mentioned in section 2.1.

Figure 6. Comparative upconversion emission spectra of the Yb^{3+} - Er^{3+} co-doped La nanostructures prepared by AODTP method (dotted line) and catechin method (solid line).

(Yb^{3+} , Er^{3+}) have been employed. Host material with low-phonon energy and the matching level of excitation energy and RE energy levels play a significant role in the energy conversion efficiency. Among REs materials, REs fluorides are more prominent for their low phonon energy, photochemical stability, and high luminous stability.⁵⁵⁻⁶¹

The photoluminescence properties of Yb^{3+} - Er^{3+} co-doped La nanostructures under 980 nm laser irradiation has been evaluated in detail. The excitation spectra of La nanostructures co-doped with Yb^{3+} (20 mol%) with varying Er^{3+} ions concentration (1, 2, 3, 5, 7, 10 mol%) and Er^{3+} (2 mol%) with varying Yb^{3+} ions concentration (5, 10, 15 mol%) are shown in Figures S3 and S4.

The absorption spectra of annealed F5Y2EA possess five absorption bands as shown in Figure 5. The absorption band at ~ 974 nm is attributed to the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition of Yb^{3+} ions. The remaining three absorption bands are attributed to f-f transitions from the ground-state $^4\text{I}_{15/2}$ to excited states of Er^{3+} ions. The absorption bands peaking at ~ 380 nm, ~ 402 nm and 520 nm, are attributed to the $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$, $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{3/2}$ and $^4\text{I}_{15/2} \rightarrow ^4\text{S}_{3/2}$ transitions respectively.³⁹ At this moment, it is not clear whether the parallel formation of oxides and oxyfluoride with fluorides would improve/decrease the upconversion luminescence efficiency. Comparative upconversion emission spectra of the $\text{Yb}^{3+}\text{-Er}^{3+}$ co-doped La nanostructures prepared by AODTP method (dotted line) and catechin method has been given in Figure 6. We have compared the intensities for both samples under same physical conditions. The samples have been pelletized with equal dimension. Moreover, the excitation powers and other conditions were kept constant throughout the experiment. Comparison with AODTP functionalized $\text{Yb}^{3+}\text{-Er}^{3+}$ co-doped La nanostructures (Figure 6), results in an increase of UC emission intensity, can be attributed to the presence of

catechin. To evaluate the presence of catechin on the nanostructures surface, a CHN analysis was performed for all the annealed samples. The results indicated a very small percentage of hydrogen ($\sim 1\%$) and carbon ($2\text{--}7\%$) in the samples. The presence of such minor quantities of carbonaceous material should be considered as the cause for the observed change in upconversion intensity. Thus, Catechin coated around rare earth ions modify the local ionic dipole fields which in turn affect the emission intensity. And also, Catechin acts as a carbon emission center.³¹ As a result of catechin effect, upconversion enhancement with constant dopant concentration was observed in Figure 6.³¹ Figure 7 shows the UC emission spectra of all the $\text{Yb}^{3+}\text{-Er}^{3+}$ co-doped La nanostructures excited at 980 nm laser diode. The UC emission spectra exhibit resolved and, sharp peaks with weak ultraviolet (UV), green and red emissions. Green emissions peaking at 520 nm and 545 nm correspond to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions respectively, while the peak in the red region at 655 nm corresponds to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. The UC emission observed at 410 nm is very weak because it undergoes three or four-photons UC process.^{62–64}

Figure 7. UC emission spectra of annealed $\text{Yb}^{3+}\text{-Er}^{3+}$ co-doped La nanostructures under 980 nm NIR diode laser excitation.

The concentration dependence of UC emission spectra of the $\text{Yb}^{3+}\text{-Er}^{3+}$ co-doped La nanostructures has been investigated in detail. With fixed Er^{3+} ions concentration (2 mol%) and upon variation of Yb^{3+} ions concentration (5, 10, 15 and 20 mol%), it was found that 5Y2EA possess higher UC emission intensity compared to that of other samples (Figure 7). It has also been observed that green UC emission (500–570 nm) intensity drastically decreases from 5 mol% to 15 mol% of Yb^{3+} ions and then suddenly increases at 20 mol% of Yb^{3+} ions. Red UC emission band (630–700 nm) intensity decreases from 5 to 10 mol% Yb^{3+} ions and remains unchanged at higher Yb^{3+} ions concentration. When the Yb^{3+} ions concentration was fixed at 20 mol% and the Er^{3+} concentration is varied (1, 3, 5 and 10 mol%), green

UC emission intensity decreases and red UC emission intensity remain unchanged till 5 mol% Er^{3+} ions concentration (Figure 7). At 20 mol%, Yb^{3+} and 10 mol% Er^{3+} , almost equal intensity of green and red emission were observed (Figure 8). 20Y1EA, with 1 mol% Er^{3+} ion concentration shows promising UC emission when compared to other samples of the same series.

To understand the UC emission mechanism, the upconversion emission intensity (I) has been measured as a function of infrared laser excitation power (P). For the upconversion process, I is proportional to the n^{th} power of P and expressed as $I \propto P^n$, where 'n' is the number of required photons absorbed by the emitting level. A plot of $\ln I$ versus $\ln P$ yields a straight line with slope n . For 20Y1EA samples (Figure 9 (a)), the

Figure 8. Integrated green and red upconversion emission intensity of $\text{Yb}^{3+}\text{-Er}^{3+}$ co-doped La nanostructures as a function of Yb^{3+} (1), Er^{3+} (2) ions concentration, while other dopant concentration remains constant and their corresponding G/R ratio (3) at 615 mW fixed pump power.

obtained slope n was 1.24 (655 nm) for red emission, 1.58 (545 nm) and 1.93 (520 nm) for green emissions. Pump power dependence data for different wavelengths are plotted individually and shown in Figure S5. The peak at 410 nm is attributed to the $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition. The blue UC emission band peaking at ~ 410 nm is due to three photon absorption process preceded by the Ground State Absorption (GSA), Excited State Absorption (ESA) and/or Energy Transfer (ET) processes.⁶⁵ Due to the very small intensity of the blue UC emission band, it could not become possible to monitor the slope value by using UC emission intensity versus pump power dependence study. These results show that the two-photon process is responsible for green and red upconversion emission.²⁵ The decrement in the slope values evidently reflects the existence of various processes in the co-doped phosphors such as energy transfer, non-radiative relaxation channels, etc.^{66,67} The schematic energy level diagram with various possible upconversion emission transitions have been depicted in Figure 9 (b). It is known that the Yb^{3+} ions are well

absorber for the 980 nm laser radiation due to the high absorption cross-section corresponding to the $^2\text{F}_{5/2} \leftarrow ^2\text{F}_{7/2}$ absorption transition. Thus, the Yb^{3+} ions act as a sensitizer in the Yb^{3+} - Er^{3+} co-doped system which can easily transfer its excitation energy to the Er^{3+} ions via energy transfer processes *viz.*, ET 1, ET 2 and ET 3 (Figure 9 (b)).

From the above results, overall emission color for all UCNP has been calculated according to CIE (Commission International del' Eclairage 1931 chromaticity) color space. Color coordinates of $x = 0.18$ - 0.27 ; $y = 0.69$ - 0.77 are known for their green color. Color coordinates of each sample is presented in Table S1. The observed average color co-ordinates are found in the green region of the chromaticity diagram. The color coordinate study further suggests that the prepared nanostructures are efficient for NIR to green upconverting materials.

4. Conclusions

Yb^{3+} - Er^{3+} co-doped lanthanum phosphor samples have been synthesized successfully by using catechin as morphology director and upconversion enhancer under hydrothermal conditions, followed by annealing. Improved crystallinity after annealing and square-shaped nanoplate shape increases the efficiency of NIR absorption. The absorption bands around 380 nm, 402 nm and 520 nm have been observed in UV-Vis and NIR diffuse reflectance and explained clearly. XPS spectra clearly indicate the chemical bonding nature of the formed products as a solid mixture of LaF_3 , La_2O_3 and LaOF . Enhancement in the UC emission of La nanostructures prepared by catechin was observed compared to AODTP method. Yb^{3+} - Er^{3+} co-doped La UCNs exhibit strong green upconversion emission upon excitation with a 980 nm NIR laser diode and is further confirmed by CIE chromaticity diagram. The developed nanostructures can be useful in the fabrication of the upconverting devices in NIR to Visible region, optics technology and for medical diagnosis purposes.

Supplementary Information (SI)

XRD, NIR absorption spectra and CIE color coordinates of all Yb^{3+} - Er^{3+} co-doped LaF_3 UCNs are available at www.ias.ac.in/chemsci.

Acknowledgements

VT would like to thank the Department of Science and Technology (DST), Govt. of India for the INSPIRE- Senior Research Fellowship and SURE project. CSIR-CLRI communication number 1218.

Figure 9. (a) UC emission intensity (at different wavelengths) as a function of pump power for F20Y1EA under 980 nm NIR excitation. Pump power dependence data for different wavelengths are plotted individually and shown in Figure S5. (b) Schematic energy level diagram for Yb^{3+} - Er^{3+} co-doped system under 980 nm laser diode excitation. Laser Power is in mW.

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