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Sodium yttrium fluoride based upconversion nano phosphors for biosensing

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Sodium yttrium fluoride based upconversion nano phosphors for biosensing

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Abstract

In the present study, $NaYF_4$-Yb^{3+}/Er^{3+} having the composition $NaYF_4$-18%Yb^{3+}/2%Er^{3+} and $NaYF_4$-20%Yb^{3+}/2%$Er^{3+}$with and without the addition of PVP (polyvinyl pyrolidone) have been synthesised by a solution method using NaF, yttrium nitrate, ytterbium nitrate and erbium nitrate as precursors. Upconversion spectra of prepared nanomaterial under 980 nm laser excitation have been studied. The variation in upconversion spectra with new born calf serum and myoglobin has been studied. Myoglobin (Mb) may be helpful when used in conjunction with other cardiac markers for rapid determination of acute myocardial ischemia, especially in patients with a typical chest pain or nonspecific ECG changes. The variation of UC fluorescence with addition of Mb indicates the suitability of using $NaYF_4$ based UC nanoparticles in cardiac marker detection. The detailed study is currently under progress.

1. Introduction

Rare earth based materials are strongly fluorescent, low in toxicity and readily synthesised in water which greatly facilitates further biofunctionalization. Hence their biological applications have been reported favourably in recent years. The luminescence of lanthanide doped inorganic materials/nanoparticles is characterized by narrow emission band widths determined by the lanthanide ions, which when used in conjunction with different dopant ions and matrices can generate different emission colours. At the same time, lanthanide doped nanoparticles offer substantial advantage over lanthanide chelates such as high photochemical stability and long fluorescent life time up to several milliseconds. Another unique feature of lanthanide doped phosphors is their ability to emit photons in the visible range after being excited with infrared light, in a process known as upconversion. Upconversion fluorescence labels possess several distinct advantages compared to commonly used down-converting phosphors.

(i) A low optical background is expected due to the absence of autofluorescence of biomolecules upon infrared radiation
(ii) Due to the large wavelength separation between excitation and emission, the optical train is very simple and so there is no need for time resolved detection and
(iii) Simultaneous detection of multiple analytes can be realized since different colours of visible light can be obtained from different upconversion phosphors excited by the same IR laser.

The most efficient UC mechanisms are present in solid-state materials doped with rare-earth ions. Lanthanide-doped upconversion materials, which can convert near-infrared lights to visible lights, have attracted growing interest because of their great potentials in biomedical engineering. However, it remains a grand challenge to manoeuvre the intensity ratio between different emission lines and enable tunable upconversion functions. However many previous upconversion phosphors used for biological labelling are somewhat too large in size and thus cannot be used for the sensitive analysis of moleculs such as DNA, RNA, or protein biomarkers. Accordingly nano sized upconverting phosphors have received considerable attention. Rare earth fluorides, $NaYF_4$ in particular are regarded as ideal host materials of low phonon energy and high photochemical stability. And tuneable upconversion emission is feasible with doping of various lanthanide ions. Among various fluoride host low phonon energy $NaYF_4$ doped either with Yb^{3+}:Er^{3+} or Yb^{3+}:Tm^{3+} trivalent rare earth ions, is recognized as one of the most efficient host for the infrared-to-visible upconversion processes [1-2]. The IR to visible UC particles offer a wide range of technological applications in solid state lasers, three dimensional flate panel displays, energy efficient photovoltaic devices biomedical imaging and photodynamic therapy applications [3-8]. Different synthesis procedures have been adapted to synthesis various upconversion systems and upconversion properties of many such systems for various applications have been studied previously [9-12]. In the present paper an attempt has been made to synthesise $NaYF_4$/Yb-Er system with different Yb^{3+}:Er^{3+} concentration using a simple solution method. PVP has been used as an additive in order to enhance biofuctionalize the material for final applications. The variations in upconversion fluorescence with different Yb^{3+}:Er^{3+} concentration with and without PVP have been dealt with. Initial trials for utilizing the nanophosphors for detection of myoglobin and new born calf serum have been dealt with.

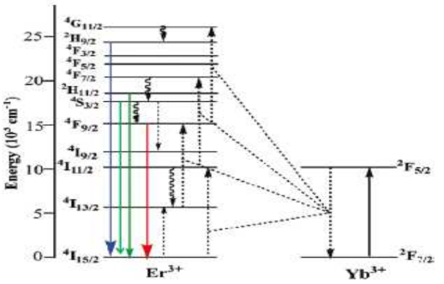


Fig. 1 UC mechanism – Energy level diagram of Yb^{3+}:Er^{3+} system

2. Experimental

For synthesizing the NaYF4/Yb^{3+}/Er^{3+} compositions, NaF (Merck Chemicals, India) in H_2O/EtOH mixture has been added to the rare earth nitrates viz. $Y(NO_3)_3.6H_2O$ (Sigma Chemicals, USA), $Yb(NO_3)_3.5H_2O$ (Sigma Chemicals, USA) and Er $(NO_3)_3.5H_2O$ (Sigma Chemicals, USA). To get 1gm of an ideal composition $NaYF_4$-18%molYb^{3+}/2mol%Er^{3+}, 1.5004 g $Y(NO_3)_3.6H_2O$, 0.4116g $Yb(NO_3)_3.5H_2O$ and 0.0434 g of $Er(NO_3)_3.5H_2O$ is well mixed in 50ml of deionized water and added to a solution of NaF (0.08192 g in 80 ml of 80:20 v/v H_2O/EtOH mixture) and stirred for around 5 hours at RT. The mixture is then centrifuged, washed around 4-5 times with EtOH and then with deionized water and the slurry after decantation is heated to 60 °C by keeping in an air oven. The dried powder is collected and used for further characterisation. For PVP added composition 25 wt% of PVP is added after homogenization of other reagents. The PVP incorporated slurry is stirred for 5-6 hours and centrifugation, washing and drying has been done as for the undoped samples. Following a similar procedure, a composition $NaYF_4$-20mol%Yb^{3+}/2mol%Er^{3+} with and without PVP additive have been synthesised. The change in upconversion fluorescence with the addition of new born calf serum and Mb has been observed, as a part of detection trials.

The fluorescence upconversion has been measured by exciting the sample at 980 nm followed by measuring the emission in the 400 nm-900 nm range at 400 mA using a Spectrofluorimeter (Edinburg Instruments Ltd, UK) equipment. The TEM has been done using a Transmission Electron Microscope (Philips CM 200 High Resolution FEGTEM, UK). The phases of the compounds have been analysed using an X-ray diffractometer (Siemens, Germany) in steps of 0.02° in the 2 theta range 10-70° with a count time of 2 seconds.

3. Results

The nanoclusters are clearly observed in the TEM images of selected samples as shown in Fig.2. It is also seen that more agglomeration is observed in samples with PVP, while nanoparticles are clearly seen in the agglomerated clusters of unmodified samples. The nanocrystallinity is also evident from the diffraction pattern.

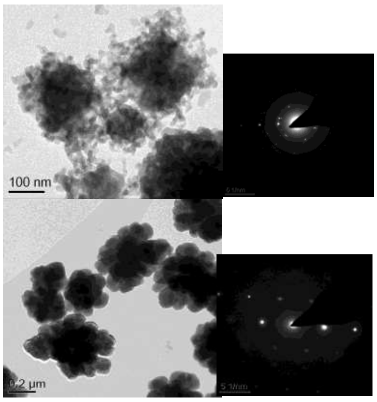
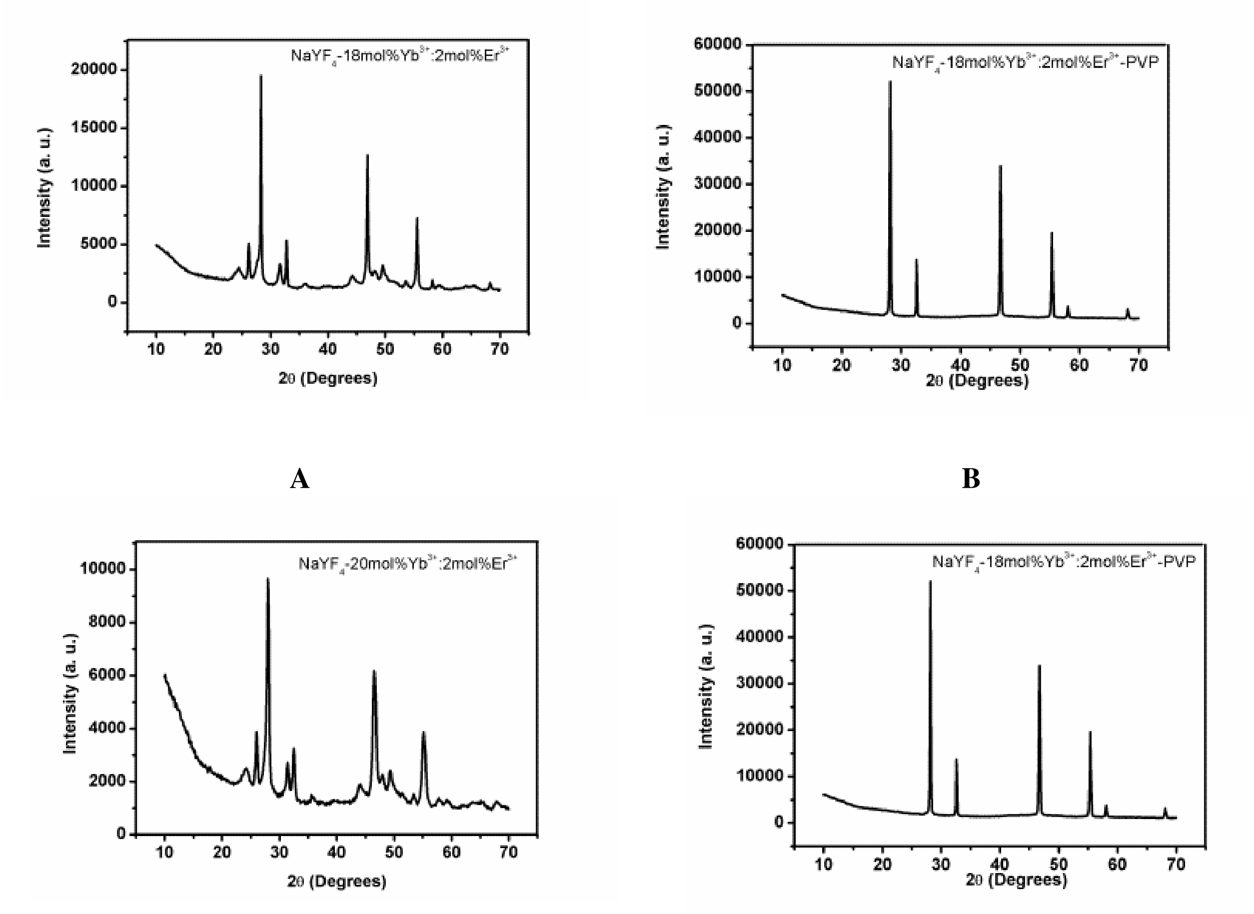


Fig. 2. TEM images of (A) NaYF4-18mol%Yb3+:2mol%Er3+ (B) NaYF4-18mol%Yb3+:2mol%Er3+PVP



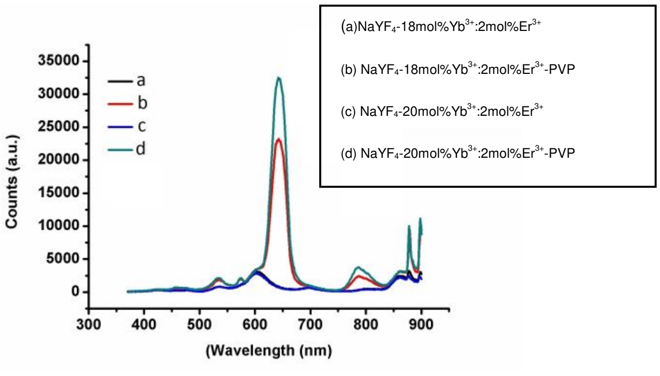
A **B**

C **D**

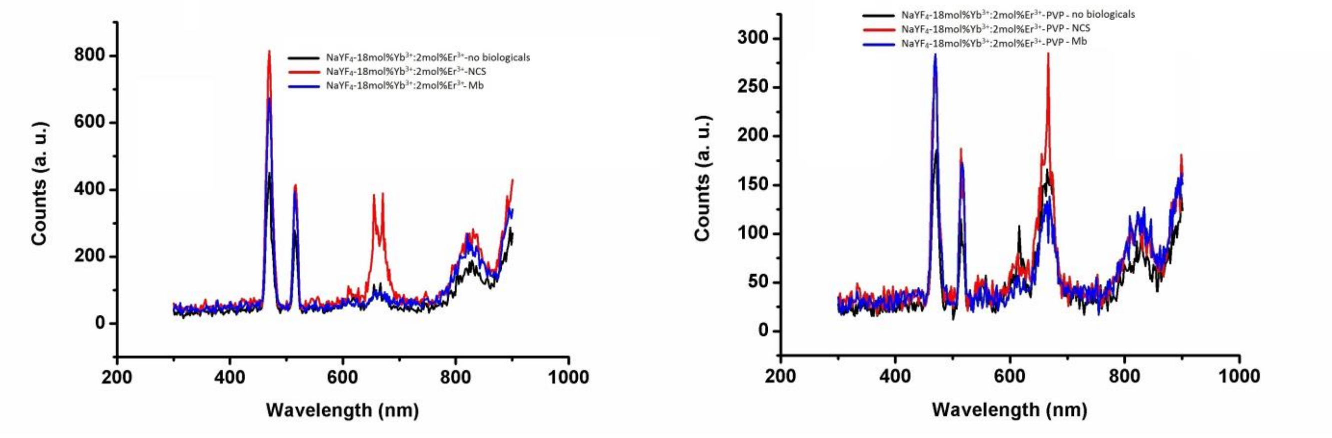
Fig.3 XRD patterns of (A) $NaYF_4$-18mol%Yb^{3+}:2mol%Er^{3+} (B) $NaYF_4$-18mol%Yb^{3+}:2mol%Er^{3+}-PVP (C) $NaYF_4$-20mol%Yb^{3+}:2mol%Er^{3+} (D) $NaYF_4$-20mol%Yb^{3+}:2mol%Er^{3+}-PVP

X-ray diffraction patterns (Fig. 3) show phase pure α- $NaYF_4/Yb^{3+}/Er^{3+}$, for PVP modified samples while mixed phases are observed in the unmodified samples.

Fig. 4 shows the fluorescence upconversion spectra of the selected $NaYF_4/Yb^{3+}/Er^{3+}$ based powder samples. It is observed that sharp peaks having very high intensity has been observed for PVP modified samples especially in the 600-700 nm range ($^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ions). Significant change is seen in the peak at ~900nm. The peaks at ~800 nm also shows significant increase in PVP modified samples while the intensity is almost zero for unmodified samples. The results show PVP considerably enhances the UC of $NaYF_4/Yb^{3+}:Er^{3+}$ system. But for aqueous



A



B C

Fig. 4: UC fluorescence spectra of (A) Samples with no biologicals (B) &(C) Sample with NCS and Mb and with out biologicals (aqueous solution)

solutions PVP is not giving much enhancement of fluorescence. But when comparing aqueous solutions with and without biologicals, the peaks observed in the range 400-550 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$) is considerably enhanced when NCS and Mb is added to the system, while the peak in the range 600-800 nm shows more sharpness in presence of Mb. While considering the peaks at 800-900 nm, Mb and NCS added samples show a little higher fluorescence. The variation in fluorescence with addition of biomolecules can be a tool for detection. Further optimization is required for elucidating a standardized procedure for detection.

4. Conclusion

Nano - $NaYF_4$-Yb^{3+}:Er^{3+} having various Yb^{3+}:Er^{3+} concentration have been synthesised by a wet chemical method. TEM picture shows the nano nature of the samples, with more agglomeration for PVP modified samples. It is observed that PVP modified samples show better UC fluorescence compared to unmodified samples. XRD shows pure cubic phase for PVP modified samples. UC spectra of the synthesised samples and possibilities of using nano – $NaYF_4$-Yb^{3+}:Er^{3+} samples in the field of biosensor have been established using new born calf serum and calf myoglobin as examples.

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