Synthesis and Upconversion Emission of NaYF₄:Er/TiO₂/ Ag Core-Shell Nanocomposites

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Abstract. The synthesis of core/shell NaYF₄:Er/TiO₂/Ag (NEA) hybrid nanostructure was prepared by the thermal decomposition process which involves Polyvinylpyrrolidone for dissolving precursors to form core NaYF₄:Er. However, TiO₂ and silver nanoparticles (AgNPs) shell were deposited on the core nanocrystal using Tetraethyl orthotitanate (TEOT) and AgNO₃ to obtain core-shell structure. The Uv-Vis-Nir absorption spectra for identification surface plamon band and the core-shell nano structural analysis were studied. Upon 808 nm laser diode excitation to NETA samples exhibit mainly green upconversion enhancement which remarkably two times and lesser red emission intensity has been marked. Through the interaction of Er³⁺ with SPR of AgNPs leads to enhance green band and it may be proven potential material for application in bioimaging. The presences of AgNP shell on nanocrystal of nanocomposite and upconversion mechanism related to enhancement were discussed.

INTRODUCTIONS

In recent year, upconversion emission of rare-earth (RE) ions doped nanocrystals with silver nanoparticles (AgNPs) doped materials have been much investigated because of their promising optical properties and potential application for sensor and bioimaging [1-4]. This can be realized by nanocomposites materials generally core/shell structure to form of RE ions doped nanocrystals with nanoparticles including surface effect and minimize quenching that would be separated in space from the emission centres. In reality, both homogeneous and inhomogeneous core/shell structures have been synthesized and examined [5-6]. One of the Hexagonal-phase sodium yttrium fluoride (NaYF₄) is known as the most efficient host materials and [7,8] widely studied. Schietinger et al observed enhancement upconversion from a single NaYF₄:Yb³⁺/Er³⁺ nanocrystal coupled with gold spheres [9]. Zhang et al reported the upconversion enhancement of hexagonal NaYF₄:Yb³⁺/Tm³⁺ nanocrystals coupled with gold nanoparticles or nanoshells [10]. In this structure, the absorption strength of the RE nanocrystal is enhanced by surface Plasmon resonance (SPR) local field effect by nearby metal AgNPs. Yuan et al [6] prepared the NaYF₄: Yb,Er@SiO₂@Ag nanostructures to modulate the upconversion luminescence. Saboktakin et al [7] fabricated a metal oxide (Al₂O₃) nanocrystals structure to investigate the spacer thickness and the enhanced upconversion emission. Thus size and shape of nanocrystals and reaction time controlling for the thickness of the shell is remain challenged in a nanostructure to investigate the strong upconversion by 980 nm and 808 nm excitation.

In this paper, we report the synthesis of NaYF₄: Er³⁺ nanocrystal in form of core-shell NaYF₄: Er/TiO₂ (NET) and NaYF₄: Er/TiO₂ @Ag (NETA) nanocomposites using Polyvinylpyrrolidone by thermal decomposition method and followed by a TiO₂ and AgNO₃ coating for water dispersibility. The Uv-Vis-Nir absorption spectra, TEM, photoluminescence and upconversion emission were applied to characterize these samples.

EXPERIMENTAL METHODS

First NaYF₄:1%Er nanocrystals were prepared by thermal decomposition process for which first 99.9% pure chemicals Y₂O₃ and Er₂O₃ were separately dissolved in dilute HCl to obtain YCl₃ and ErCl₃. Then, it was mixed and heated to evaporate the water and excess HCl. Using 10 ml Ethylene glycol was added to dissolve the RECl₃ powders (RE = 0.79 mmol Y, 0.01 mmol Er). Using Polyvinylpyrrolidone (PVP, 0.01 g) and NaCl (1 mmol) were
added and the solution was heated to 80°C to form a homogenous solution. Take 4mmol of NH₄F was dissolved in 10 ml of ethylene glycol at 80°C and then NH₄F solution was added dropwise to the RECl₃ solution under stirring at room temperature. After that final mixture was stirred continuously for 2h, and then transferred into an autoclave and maintained at 176°C for 12h. After cooling to room temperature, the product obtained by centrifugation was washed three times with ethanol and dried at 60°C for 2 h. For the TiO₂ coatings on NaYF₄: Er nanocrystals was carried out through hydrolysis of Tetraethyl orthotitanate (TEOT) chemical. For that NaYF₄ nanocrystals (0.015 g) were dispersed in ethanol (15 ml) by ultrasonic treatment and mixed with TEOT (1.5 mmol) under stirring. Ethanol (15 ml) containing water (4.5 mmol) was added dropwise to the above solution. One-third of the final solution (30 ml) was taken out and centrifuged at different reaction times. The separated NaYF₄/TiO₂ core/shell nanoparticles were rinsed with ethanol and dried at 60°C for 2 hrs. The upconversion nanocrystals were re-distributed in 3.0 mL of 0.5mM and 1.0mM of AgNO₃ solution, trailed by mixing 60 mL of 100mM ethanolamine solution. The resulting mixture was agitated for 1 hr at the rate of 200 rpm at 30°C. After that NaYF₄: 1%Er/TiO₂/Ag nanocrystals were again centrifuged and cleaned with ethanol and water many times [11].

The absorption spectra of the glasses were recorded in the range 300-1200nm using UV/VIS/NIR spectrometer Varian Model 5000. The Transmission Electron Microscope (TEM) operating at 200kV was employed to confirm the presence of the core-shell structure formation of NETA sample. The upconversion emission spectra were obtained in the range from 400nm to 700 nm by using a model Ava Spec 2048 Avantes, Fibre Optics Spectrometer excited by 808nm CW diode laser.

RESULTS AND DISCUSSIONS

The UV–Vis-Nir spectra of aqueous suspensions of prepared NaYF₄: Er/TiO₂ and NaYF₄: Er/TiO₂/Ag nanostructures samples which annealed at 150°C for 1h are shown in Figure 1. To better visualize of optical properties of the fabricated TiO₂ and Ag-modified nanostructures (NTEA) leads to an overall increase in the refractive index of their local dielectric environment [12]. We have observed large red-shift absorption of the band the plasmon resonance with overlapped of Er³⁺ ions main peaks. Thus NTEA has a broad absorption band which increased with the presence of due to AgNPs formation in the nanocomposite. In this way, nanocomposite NTEA has a maximum of redshift absorption bands may also be recorded without Er³⁺ ions doped samples of NTA nanocomposite.

To further confirm the core-shell structured of samples, TEM observations were performed. Figure 2 show the TEM micrographs of the core-shell samples indicates the core and shell domains of the samples can be distinguished clearly due to their different electron penetrabilities. For 0.5 mmol AgNPs content NTEA sample shows a nearly spherical shape for both the core and shells with sizes of 78 and 94 nm respectively.

The intense green upconversion emission is observed under 808nm laser excitation of NETA with and without AgNPs shell nanocomposite for their comparison as shown in Figure 3. On increasing the concentration 0.5mM to 1.0mM of AgNO₃ in NTEA sample that emits green at 550 nm (transition ⁴S₉/₂→⁴I₇/₂) intensity increase due to transverse SPR and red upconversion ⁴F₉/₂→⁴I₇/₂ intensity due to longitudinal SPR has been observed [13]. Thus,
maximum 2-fold green upconversion enhancement is measured, which is due to local field or/and energy transfer (ET) from Ag NPs to Er$^{3+}$ ions in NTEA sample. Also more likely scattering or re-absorbance of the excitation light may lower the 550 nm green emission intensity which is around plasmon band. However, the ability of green intensity enhancement can be maintained with increases annealing duration of NETA nanocomposite.

**FIGURE 3.** Upconversion spectra of NTEA samples

**FIGURE 4.** Energy-level pathways of AgNP- Er$^{3+}$ in NTEA Core-shell

Figure 4 shows possible energy transfer from AgNPs to Er$^{3+}$ ions in NETA core-shell samples. As single RE ions in nanocomposite the possible ground state absorption of Er$^{3+}$ ions is taken place by 808nm photon excitation with association of SPR waves and excited to the $^4$H$_{9/2}$ level then decay to $^4$I$_{11/2}$ followed by excite state absorption (ESA) to the $^4$F$_{5/2}$ state. Then after quickly decays non-radiatively to the $^2$H$_{11/2}$ and $^4$S$_{3/2}$ levels [14], from which emit green emission transition to $^4$I$_{15/2}$. Besides, the lesser red emission intensity comes from non-radiative populated $^4$F$_{0/2}$ level which decay to ground level by emitting the 635nm photon. Other possible upconversion processes such as radiative and non-radiative decays from AgNPs ions to $^4$I$_{11/2}$ level of Er$^{3+}$ ions and cross-relaxation may exist in Er$^{3+}$ ion pairs, it lead to major quenching mechanism at high concentrations of Er$^{3+}$ [15] is possible. Thus upconversion enhacement in NETA nanocomposite could be due to SPR of AgNPs and it field enhancement effect with energy transfer from AgNPs to Er$^{3+}$ happened effectively.

**CONCLUSIONS**

We have prepared core/shell NaYF$_4$:Er/ TiO$_2$/Ag nanocomposite with variation of Ag NO$_3$ from 0.5 to 1.0 mmol and fixed 1mol% of Er$^{3+}$ ions by the thermal decomposition process. The Absorption spectra show SPR band is present in the range of 400-600nm and TEM measurement confirms the presence of core-shell form exists in the nanocomposite. The observed result indicates that at 808 nm excitation of core-shell of NTEA produces green upconversion enhancement as compare to red, which is about two orders for 1.0 mmol content AgNPs in NETA samples. Taking into account the observed green emission based on the energy transfer process between shell Ag NPs and Er$^{3+}$ ions that involves at least two photons. Thus the core-shell NaYF$_4$: Er/TiO$_2$/Ag nanocomposite favour the enhancement of green upconversion emission may be useful for bioimaging applications.

**ACKNOWLEDGMENTS**

The work is supported by DST- SERB Project grants no EMR/2015/001017. The authors would like to thanks to CIF, Pondicherry University, SICART, VV Nagar, India for providing the characterization Facilities.
REFERENCES