Monitoring of the luminescence properties of the upconversion YVO₄:Yb, Er nanoparticles during preparation processes

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Abstract. We have fabricated the upconversion nanoparticles (NPs), which are nanocrystallites of 10 nm, doped with Yb³⁺ and Er³⁺ ions, prepared through hydrothermal method. Monitoring of their photophysical properties had been realized at different fabrication stages by using electron microscopy and luminescence spectroscopy under photoexcitation of the NPs with the 100 mW laser at 980 nm wavelength. The performed monitoring allows us to observe dramatic changes in the upconversion properties of the NPs during the sequence of the fabrication stages and revealed very strong correlation between the NPs’ upconversion efficiency and their structural specificities.

1. Introduction

Today high efficient upconversion nanoparticles (NPs) have been wildly used in bioimaging [1-3], optogenetics [4-7], drugs delivery [8, 9], photoactivation [10, 11], theranostics [12-14] and photodynamic therapy [15-18]. As is known, lanthanide ions Yb³⁺ and Er³⁺ doped into NPs are capable of converting near infrared radiation into visible luminescence. The upconversion process occurs as a result of energy transfer from Yb³⁺ ions with high absorption cross section at 980 nm to Er³⁺ ions. Real metastable states involved in energy transfer in the lanthanide ions have microseconds lifetimes defining high probability of two-photon processes [19, 20]. According to [21-23], upconversion is realized as successive processes of near infrared light absorption by Yb³⁺ ions via the ²F₇/₂→²F₅/₂ transition followed by the energy transfer from the ²F₅/₂ level of Yb³⁺ ions firstly to the ⁴I₁₁/₂ level of the Er³⁺ ions and finally
to the $^4F_{7/2}$ level (see figure 1). After that, various radiative and non-radiative transitions responsible for relaxation of Er$^{3+}$ ions depopulate $^2H_{11/2}$ and $^4S_{3/2}$ levels.

![Energy-level diagram showing upconversion processes in NPs.](image)

**Figure 1.** Energy-level diagram showing upconversion processes in NPs. Solid arrows indicate radiative processes, dashed arrows and lines are energy transfers and non-radiative transitions.

Upconversion efficiency strongly depends on the rate of multiphonon transitions and non-radiative relaxation. The crucial factor is luminescence quenchers attached to surfaces or defects of NPs [24]. Therefore, it is of great importance to realize detailed control of such processes for design of new NPs insensitive to quenchers on their surfaces and highly suitable for biological applications. With this aim, we focus on monitoring the efficiency of upconversion luminescence at different fabrication stages of YVO$_4$ NPs doped with Yb$^{3+}$ and Er$^{3+}$ ions to observe structural transformations and reveal their effects on luminescence intensity. Our choice of YVO$_4$: Yb, Er NPs arises from the fact that they are less sensitive to luminescence quenchers in water solutions as compared, for instance, with fluoride counterparts, taking into account that bright upconversion emission of NPs in biological tissues is a key factor for their successful using in broad range of biological applications.

2. Measurements
An EVO 50 XVP (Carl Zeiss) electron microscope was used for studying surface morphology of NPs. NPs dispersed in water were dried on the quartz plate, then the sample prepared through this process was placed in the electron microscope. The obtained results are shown in figures 2a, 3a and 4a.

The luminescence of the investigated NPs (the spectra shown in figures 2b, 3b and 4b) was excited at 980 nm with the MicronLux laser of 100 mW output power. The pump beam was focused by $20 \times$ microscope objective on the sample from below through the object-plate (the beam power on the sample was about 50 mW). The luminescence emission had been collected with the objective NA=0.70 from the upper surface of the sample, where NPs were positioned. We used the dichroic mirror and the FELH-800 filter to separate out the luminescence from the pump radiations. The filtered radiation was coupled to the multimode fiber with an aspheric short-focus lens, and out of one with $4 \times$ micro-objective, after that it was focused with a long-focus lens on the entrance slit of the M266 monochromator. The recording of the luminescence spectra had following specifications: the exposition was 34 s, the number of frames used in averaging was 74, and the width of the entrance slit was 400 µm. The luminescence spectra were corrected by taking into account the signal recorded with the clear quartz plate.

3. Synthesis and monitoring
The fabrication of the upconversion NPs was based on a hydrothermal method as described below. The water solution of Y(NO$_3$)$_3$, Er(NO$_3$)$_3$ and Yb(NO$_3$)$_3$ with concentration of 0.1, 0.002 and 0.02 mol/l
respectively was slowly added to the water solution of Na$_3$VO$_4$ with 0.1 mol/l concentration under constant stirring at room temperature. As a result we have obtained a white precipitate which indicated that YVO$_4$:Yb, Er NPs had been synthetized. After the remained solution was dried, a powder-like substance was obtained.

As one can see in figure 2a, NPs at this fabrication stage are sticking together in structureless amorphous formations of 5 – 50 nm sizes. The experiments evidenced that the NPs of such type exhibit no upconversion properties: we observed no luminescence signal in the range of 500 – 700 nm upon an excitation by 980 nm radiation (see figure 2b). Apparently, the main reason of complete luminescence quenching is amorphous structures of the NPs, which, firstly, prevent an energy transfer from Yb$^{3+}$ ions to Er$^{3+}$ ions and, secondly, due to numerous structural defects provide excellent conditions for fast non-radiative relaxation.

**Figure 2.** Electron microscopy image of amorphous YVO$_4$:Yb, Er NPs after the first fabrication stage (a). The noise and the instrument function with no luminescence signal were observed under irradiation of the amorphous NPs at 980 nm (b).

After synthesis of amorphous NPs we proceeded to next fabrication stage involving calcinations for 1 h at temperature of 500 °C and following annealing for 10 min at temperature of 1000 °C. As shown in figure 3a, the fabricated NPs are the nanocrystallites of the 10 – 100 nm sizes. They exhibit some
upconversion properties: under excitation by 980 nm radiation we recorded two very weak luminescence bands in the ranges of 540 – 575 nm and 645 – 720 nm, which have to be associated with Er$^{3+}$ ions emissions corresponded to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ radiation transitions. This fact indicates a two-photon excitation mechanism of the luminescence along with an energy transfer processes between lanthanide ions. It is worth to note that the luminescence band at 660 nm is more intensive. We believe it happened because of efficient non-radiative $^4S_{3/2} \rightarrow ^4F_{9/2}$ transition, which quenched luminescence in the range of 550 – 575 nm and populated the $^4F_{9/2}$ level. Low intensity of the band at 660 nm is an experimental evidence for efficiency of the non-radiative relaxation. It is natural to expect that main reason of the observed fast multiphonon intraionic transitions is high concentration of structural defects in nanocrystallites.

The third fabrication stage of NPs was as follows. After hydrothermal synthesis of amorphous NPs (the first stage) we prepared colloidal silica sol by heating tetraethylorthosilicate, ethanol and distilled water for 1 h at pH = 1.25 and temperature of 60°C. Then amorphous NPs were incorporated into the silica sol with dispersed polymer (PE6800) (the molar ratio is V/Si/PE6800 = 1:5:0.05). After drying, we got mesoporous silica network encapsulating NPs and then carried out calcination for 1 h at 500 °C and annealing for 10 min at 1000 °C. The remained silica matrix was removed after 3 h treatment in hydrofluoric acid with the molar ratio of HF/Si = 9:1.

Figure 4a shows the obtained NPs after the third fabrication stage. One can see that their sizes are less than 10 nm and they are much more homogeneous as compared to the NPs shown in figure 3a. The experiments indicated that the obtained NPs exhibit bright luminescence under excitation by 980 nm radiation, i. e. they have efficient upconversion properties. In addition, the absence of character emission band at 600 nm corresponding to the radiative $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition confirms indirectly the upconversion efficiency. We believe that this fact should be attributed to low rates of the non-radiative transitions between levels of the lanthanide ions. The gap between the $^4S_{3/2}$ and $^4F_{9/2}$ levels is about 3100 cm$^{-1}$, and thus it needs more than three phonons of the YVO$_4$ matrix with 880 cm$^{-1}$ energy to realize the transition via multiphonon mechanism.

**Figure 4.** Electron microscopy image of YVO$_4$:Yb, Er NPs after the third fabrication stage (a). The luminescence signal observed under irradiation of the NPs at 980 nm (b).

Most probably, the structure of the NPs has low concentration of defects, which could be the sources of high-energy phonons and manifold increase the rates of non-radiative transitions. Thus, the main relaxation channel of the excited Er$^{3+}$ ions is the radiation emission at the range near 550 nm that results in the bright luminescence. It is not possible to evaluate the difference between the upconversion efficiencies of the NPs shown in figures 3b and 4b. A very rough estimation indicates that the luminescence intensity in the range near 550 nm of the NPs shown in figure 4b is at least two orders of magnitude larger than that of the NPs shown in figure 3b. It evidences the dramatic difference in
photophysical properties of different NPs determined by their structures. At the same time, it allows us to consider the high efficient upconversion NPs fabricated after third stage with the size of 10 nm as promising nanoprobes for wide range of biological applications (such as bioimaging, optogenetics and etc.).

Acknowledgments
The synthesis of NPs was supported by Act 220 of the Russian Government (Agreement No. 14.W03.31.0028 with the host organization ZPTI of KazanSC of RAS). The optical measurements were carried out with financial support of Russian Foundation for Basic Research (RFBR, Grants No. 19-02-00569, and No. 20-02-00545) and the electron microscope study was supported by Program of the Presidium of RAS “Actual problems of low temperature physics”.

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