Luminescence properties of YVO₄:Yb,Er nanoparticles dispersed in water

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Abstract. We have synthesized YVO₄: Yb, Er nanoparticles in the size range of 100-500 nm, which form aqueous colloidal solutions and are luminescent when excited by femtosecond light pulses at a wavelength of 263 nm. It was established that the luminescence occurs due to the emission of Er³⁺ ions in characteristic spectral lines at 525 nm and 550 nm. However, an effective quenching channel for metastable levels of Er³⁺ ions is evident, so that the characteristic luminescence line of Er³⁺ ions in the 660 nm region is absent. We associate this quenching channel with a large concentration of lattice defects with possible localization of high-frequency quenchers.

1. Introduction

Technologies minimizing the invasive intervention and providing the ability to stimulate certain neurons in deep brain tissues remotely are of significant interest in the study of neural systems and clinical treatment of neurological abnormalities [1-7]. The major drawback of most methods is an optical fiber introduced into the brain tissue to transport blue or green photons for the activation of ion channels. The use of upconversion nanoparticles, which absorb in the near-IR and emit in the green region, provides a non-invasive efficient way to activate ion channels [8]. In this case, low-energy IR photons can penetrate deep into biological tissues, and afterwards be converted to high-energy visible range photons in upconversion process in nanoparticles [9,10].

Oxide and fluoride nanoparticles doped with Yb³⁺ or Er³⁺ ions are of particular interest for these applications, since in those the upconversion process is based on real metastable states with microsecond lifetimes [11, 12]. This causes an extremely high upconversion efficiency compared to multi-photon processes where virtual levels are involved. Thus, upconversion luminescence could be obtained with nanoparticles excited by CW laser radiation, whereas multiphoton excitation requires high-intensity laser pulses.

On the other hand, metastable states are subject to nonradiative multiphonon relaxation in the presence of high-frequency oscillators; therefore, up-conversion luminescence is usually observed in crystals with lower phonon energies [13, 14].
The particular qualities of biological environments in which nanoparticles are supposed to be introduced should also be noted. An efficient upconversion process must be sustained while a nanoparticle is in colloidal aqueous solution, with high probability of absorption of an organic quencher at its surface. An approach proposed in [15–18] allows one to synthesize defect-free YVO₄: Yb, Er nanoparticles with dimensions on the order of tens of nanometers, and the rate of non-radiative relaxation of metastable levels involved in the up-conversion process is significantly reduced. The larger size of the nanoparticles eliminates the effect of organic high-frequency quenchers absorbed at the surface on the luminescence intensity. Meanwhile, the absence of crystal defects contributes to the protection of doped Yb³⁺ or Er³⁺ ions from quenchers.

2. Experimental methods

2.1. Synthesis
Upconversion nanoparticles were prepared according to the following procedure. A solution of Y(NO₃)₃, Er(NO₃)₃, and Yb(NO₃)₃ (c = 0.1, 0.002, and 0.02 mol/l, respectively) was slowly added to a Na₃VO₄ solution (c = 0.1 mol/l) under constant stirring at room temperature. A white precipitate, corresponding to crude YVO₄:Er,Yb nanoparticles, was obtained and further purified by dialysis. A silica sol was prepared by heating tetraethylorthosilicate, ethanol, and distilled water at pH = 1.25, T = 60°C for 1 h. Crude yttrium orthovanadate particles were then incorporated into a silica sol with a dispersing polymer (PE6800) (the molar ratio of V/Si/PE6800 = 1:5:0.05). After drying, a mesoporous silica network was obtained, encapsulating the nanoparticles. It was calcinated at 500°C for 1 h and then annealed at 1000°C for 10 min. The silica matrix was removed by a 3 h treatment in hydrofluoric acid with the molar ratio of HF/Si = 9:1.

2.2. Electron Microscopy Characterization
The elemental composition and surface morphology of the samples were studied on a scanning electron microscope (SEM) “Zeiss EVO50 XVP” equipped with energy-dispersive X-ray (EDX) spectrometer “Oxford Inca Energy-350”. The EDX analysis was performed applying an accelerating voltage of 10 kV. Scanning electron microscopy and energy dispersive X-ray spectroscopy measurements were performed in order to characterize the microstructural and stoichiometric properties of YVO₄:Yb,Er nanoparticles (figures 1 and 2).

Studies have shown that the surface of nanoparticles does not contain Er atoms, which indicates their localization inside the nanoparticles. The size of nanoparticles varies in the range of 100 - 500 nm.

2.3. Emission Measurements
For optical excitation of a colloidal solution of YVO₄: Yb, Er nanoparticles, the fourth harmonic of Yb: KGW femtosecond laser with a carrier wavelength of 263 nm (pulse energy of 3 nJ, duration of 200 fs) was used. The pump beam was focused with a quartz lens onto a 1 mm thick quartz cell. The size of the pump radiation spot was approximately 50 μm. The photoluminescence emission was collected by a quartz lens with an aperture of 5 cm and a focal length of 5 cm. After that, the luminescence emission was passed through long-pass filter to eliminate scattered pump radiation, then focused with a glass lens onto the entrance slit of the MDR-12 monochromator, and detected with PMT-79 photomultiplier. The obtained luminescence spectrum is shown in figure 3.
3. Results

The luminescence spectrum in Figure 2 contains two strong structured bands in 525 nm and 550 nm regions, which are associated with Er$^{3+}$ ion emission and correspond to $^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$ and $^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$ transitions, respectively. This indicates that Er$^{3+}$ ions are mainly involved in the radiative relaxation of nanoparticles, also confirming their presence inside the nanoparticles. However, both the presence of a band in the region of 570 nm unrelated Er$^{3+}$ ions and the absence of a characteristic Er$^{3+}$ spectral line in the region of 660 nm indicates the presence of quenchers, e.g., lattice defects in nanoparticles. This indirectly confirms the apparent necessity of high-intensity femtosecond pulses for luminescence excitation (e.g. no luminescence was observed under pulsed nitrogen laser excitation (wavelength of 337 nm, pulse energy of 30 µJ and duration of 10 ns). It should also be noted that we could not detect the luminescence of the nanoparticles before the annealing procedure, because in the growth process particles with significant lattice defects are being formed. Those act as effective quenchers of metastable levels of Er$^{3+}$ ions, and annealing eliminates some of them, so it becomes possible to excite the luminescence (figure 3), with strong femtosecond pulses.
4. Conclusion

We have synthesized YVO$_4$:Yb,Er nanoparticles in the size range of 100-500 nm. It has been shown that after the annealing procedure, Er$^{3+}$ ions within the nanoparticles start to luminesce under excitation with strong femtosecond pulses at a wavelength of 263 nm. We believe that the reason for the low luminescence efficiency is a significant concentration of defects remaining after the annealing procedure. They act as luminescence quenchers, effecting in the suppression of characteristic spectral line of Er$^{3+}$ ions in 660 nm region in the recorded luminescence spectrum. Note that the implementation of the upconversion process requires long-lived metastable levels of Er$^{3+}$ ions without effective quenching channels. Thus, further research is needed in order to eliminate lattice defects in YVO$_4$:Yb,Er nanoparticles, and we expect it to allow producing efficient upconverting nanoparticles with a possible application in optogenetics.

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