Synthesis and characterization of Gd_2O_3: Er^{3+}, Yb^{3+} doped with Mg^{2+}, Li^+ ions – effect on the photoluminescence and biological applications

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INTRODUCTION

Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+} (x=0; 2.5; 4; 5; 6; 8;10; 20; 25; 50) and Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2,5% Mg^{2+} , y% Li^+ (y=0.5–2.5) nanoparticles (NPs) were synthesized by homogenous precipitation method and calcined at 900°C for 3h in air atmosphere. Powder x-ray diffraction, scanning electron microscopy, cathodoluminescence, transmission electron microscopy, energy dispersive x-ray spectroscopy and photoluminescence techniques were employed to characterize the obtained nanoparticles. We observed a 8-fold increase in red luminescence for samples suspended in DMSO solution for 2.5% of Mg^{2+} doping. The x-ray analysis shows that for the concentration of 2.5% Mg, the size of the crystallites in the NPs is the largest, which is mainly responsible for the increase in the intensity of the upconversion luminescence. But the addition of Li^+ ions did not improve the luminescence of the upconversion due to decreasing of crystallites size of the NPs. Synthesized nanomaterials with very effective upconverting luminescence, can act as luminescent markers in *in vivo* imaging. The cytotoxicity of the nanoparticles was evaluated on the 4T1 cell line for the first time.

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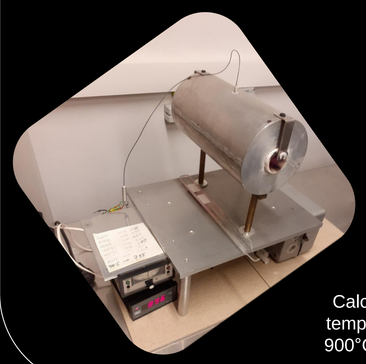
NANOPARTICLE SYNTHESIS

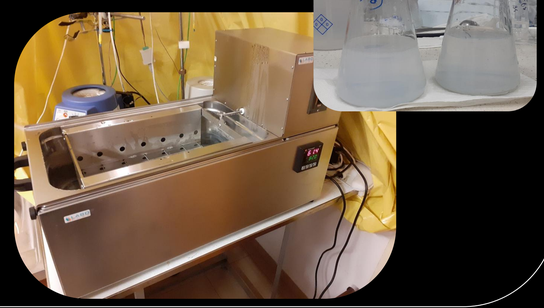
HOMOGENOUS PRECIPITATION METHOD

REDUCER
$CO(NH_2)_2$

OXIDANTS
$Gd(NO_3)_3 \cdot 5\,H_2O$
$Mg(NO_3)_2 \cdot 6\,H_2O$
$Er(NO_3)_3 \cdot 5H_2O$
$Yb(NO_3)_3 \cdot 5H_2O$

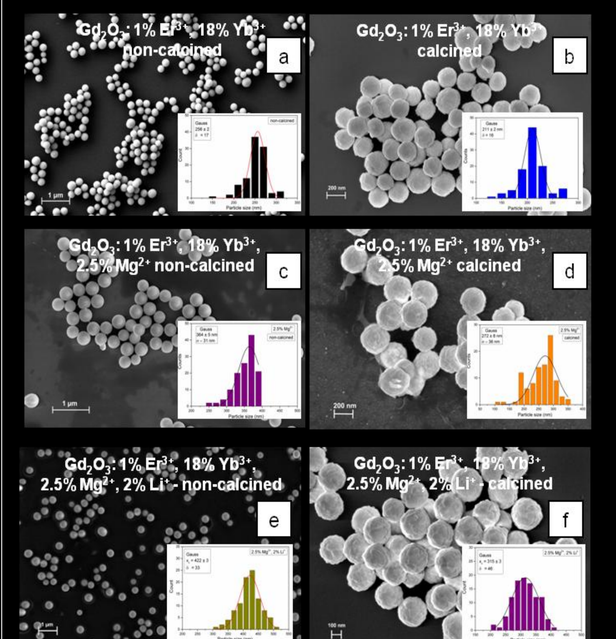
150 ml of distilled water
85°C - 2h





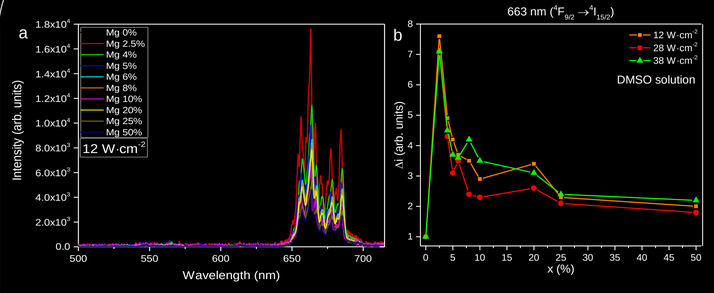
Calcination temperature: 900°C for 3 h

NANOPARTICLE SIZE BY SCANNING ELECTRON MICROSCOPY



Scanning Electron Microscopy images of a) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+} (non-calcined) b) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+} (calcined) c) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+}, x = 2.5 (non-calcined) d) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+}, x = 2.5 (calcined) e) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2.5% Mg^{2+}, y% Li^+, y = 0.02 (non-calcined) and f) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2.5% Mg^{2+}, y% Li^+, x = 0.02 (calcined). Insets: Size distribution histograms.

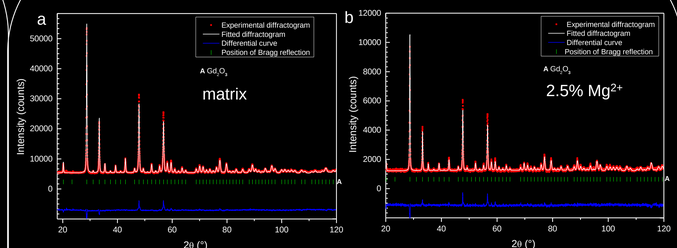
PHOTOLUMINESCENCE OF NPs SUSPENDED IN DMSO



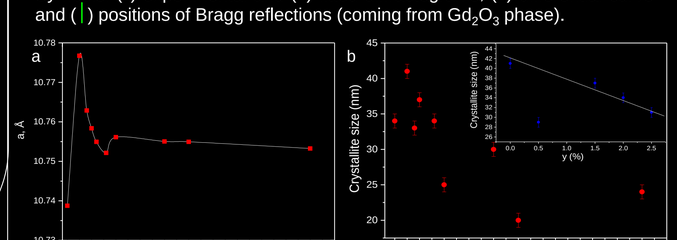
Photoluminescence of the nanoparticles suspended in DMSO solution. The spectra were measured for Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+} nanoparticles. Measurements were made in the visible area at 12 W·cm^{-2} (980 nm-continuous wave mode).

Dependence of the increase of the red luminescence (Δi) ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) efficiency of nanoparticles: Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+} as a function of magnesium ions concentration (Mg^{2+}). Measurements were carried out for three different laser power densities (980 nm – continuous wave) and for the samples suspended in DMSO. The measuring points are connected to facilitate the reading of the relationships on the graph.

X-RAY DIFFRACTION

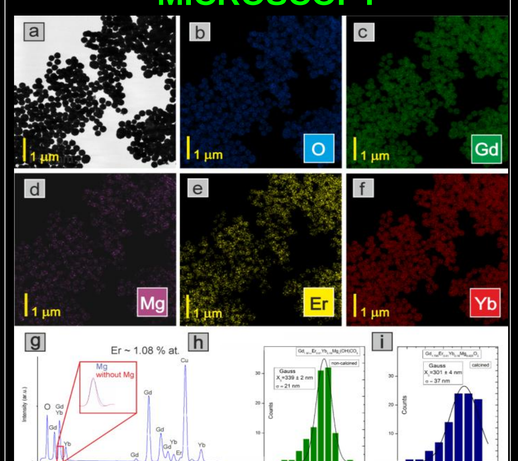


Experimental diffractograms measured for calcined (a) Gd_2O_3:1% Er^{3+}, 18% Yb^{3+} (b) Gd_2O_3:1% Er^{3+} , 18% Yb^{3+} , x% Mg^{2+} x=2.5 nanoparticles and matched by the means of the Rietveld method theoretical diffractograms Symbols: (•) experimental and (–) fitted diffractograms, (–) differential curve and (|) positions of Bragg reflections (coming from Gd_2O_3 phase).



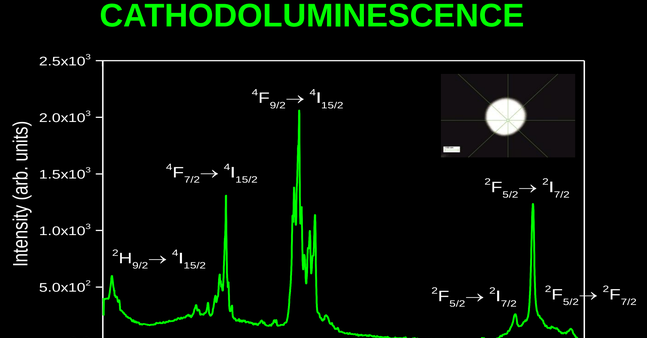
a) Parameters of the crystal structure in the Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+} determined by the Rietveld method. b) The average crystallite sizes as a function of magnesium (red solid circle) and lithium (blue solid circle, inset) ions concentration, dotted and dash lines are guide to eye.

TRANSMISSION ELECTRON MICROSCOPY



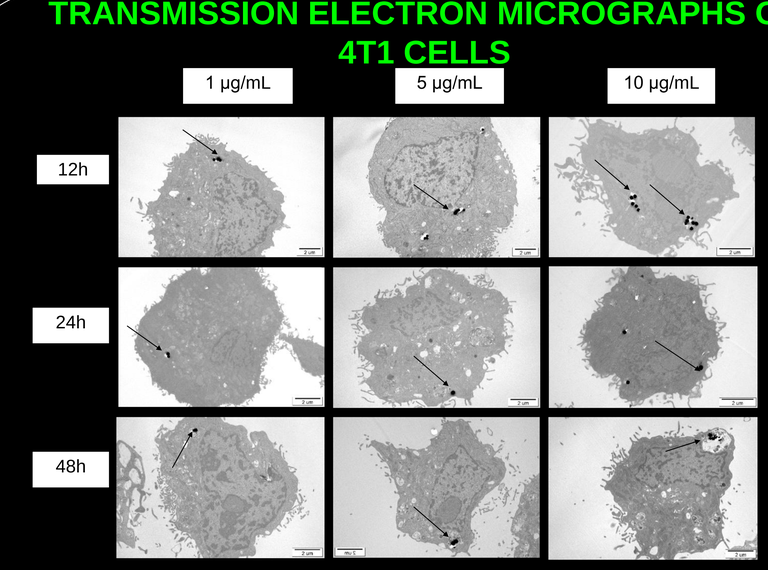
a-f) TEM elements distribution maps of Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, x% Mg^{2+}, x = 2.5 (calcined) nanoparticles, and h-i) size distribution histograms of the non-calcined and calcined NPs.

CATHODOLUMINESCENCE



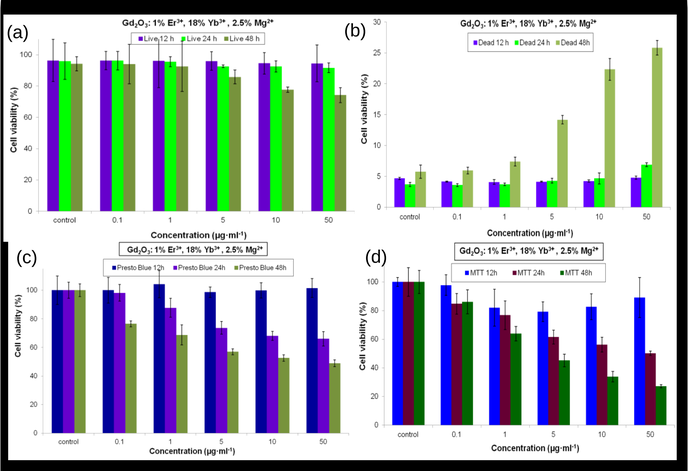
Cathodoluminescence spectra of Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2.5% Mg^{2+}, 0.02% Li^+ nanoparticles measured from 400 nm to 1100 nm.

TRANSMISSION ELECTRON MICROGRAPHS OF 4T1 CELLS



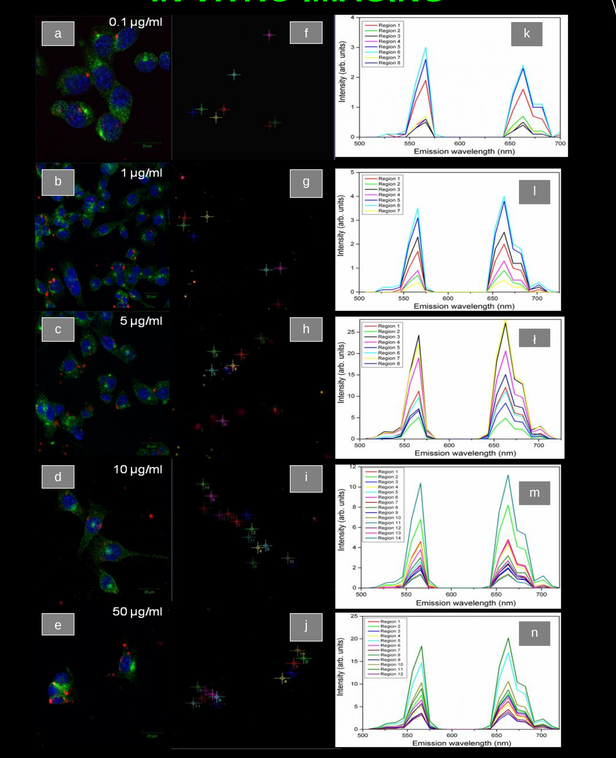
Transmission electron micrographs of 4T1 cells incubated with different concentrations: 1, 5 and 10 µg/mL respectively of the Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2.5% Mg^{2+}/PVP (339 nm) NPs for 12h, 24h and 48h.

TOXICITY TEST OF NPs



Cell viability of 4T1 cells after 12 h, 24 h, and 48 h incubation with five concentrations of Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2.5% Mg^{2+} NPs coated by PVP as determined by a-b) Live Dead assay c) PrestoBlue assay and d) MTT assay.

CELL CULTURE AND CONFOCAL *IN VITRO* IMAGING



Confocal images of 4T1 cells after 24h incubation in a solution with a, f) 0.1 µg/mL b, g) 1 µg/mL c, h) 5 µg/mL d, i) 10 µg/mL e, i) 50 µg/mL of Gd_2O_3:1% Er^{3+}, 18% Yb^{3+}, 2.5% Mg^{2+}, 0.02% Li^+ /PVP. The NPs were excited with a 980 nm femtosecond laser (observed as red spots). The 4T1 cells were marked using immunofluorescence method. Antibodies conjugated with AlexaFluor 488 dye (excited by 488 nm argon laser) were attached to the lysosomes. The signal was collected in the range from 496 nm to 570 nm (observed as a green regions). Nuclei stained with Hoechst 33342 dye were excited with a wavelength of 705 nm (blue color). The signal was collected in the range from 423 nm to 475 nm. The images are a superposition of NP luminescence, marked cells fluorescence, and nuclei fluorescence. The spectra of NPs were excited by a femtosecond laser at a wavelength of 980 nm and average laser power of 5%.

CONCLUSIONS

We showed a viable strategy of the enhancement of the upconversion luminescence in Gd_2O_3:1% Er $^{3+}$, 18% Yb $^{3+}$, x%Mg^{2+} (x=0–50) and Gd_2O_3:1% Er^{3+} , 18% Yb^{3+} ,2.5% Mg^{2+}, y% Li^+ (y=0.5 to 2.5) nanoparticles (NPs).

The NPs are single phase of bixbyite structure type and uniform composition.

The NPs exhibit effective red luminescence at 663 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) and green luminescence at 565 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$).

The obtained results reveal the cytotoxicity of the studied NPs in 4T1 cell and the cell penetration (endocytosis). To the best of authors' knowledge such observations have not been reported yet.

In this work, a correlation was observed between the concentration of magnesium ions in the starting solution, the size of nanocrystallites that nanoparticles consists of, and the intensity of upconversion luminescence. The maximum intensity of the upconversion luminescence at 2.5% concentration of Mg^{2+} ions is accompanied by the maximum size of the crystallites forming nanoparticles.

At the same time, the crystal lattice constant of Gd_2O_3 reaches its maximum. This phenomenon of lattice expansion in nanocrystallites has been repeatedly confirmed experimentally and in theoretical models.

The above facts lead to the conclusion that the increase in the intensity of the upconversion luminescence observed by us is mainly related to the increase in the size of the crystallites forming the nanoparticle, and the donor-acceptor distance has negligible influence.

The lowering of the symmetry of the crystal field around Er3+ ions also has a much smaller impact on the intensity of the luminescence in relation to the size of the crystallites. This is evidenced by a decrease in the intensity of luminescence with an increase in the concentration of Mg^{2+} ions.

When doping Gd_2O_3: Yb^{3+} , Er^{3+} nanoparticles with 2.5% Mg^{2+} and Li^+ ions, we observe a decrease in luminescence intensity in the entire range of Li^+ concentrations used. In our opinion, this is due to the fact that the addition of lithium reduces the size of the nanoparticles and the crystallites that form them.

Acknowledgements

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