Morphological control of core@shell NaYbF$_4$:Tm, Ho, Gd@NaYF$_4$ nanoparticles

Caroline D. Barreira* (IC), Emille M. Rodrigues (PG), Italo O. Mazali (PQ), Fernando A. Sigoli (PQ)

Abstract
In order to study a new methodology that will provide a better size distribution and morphology of NaYbF$_4$:Tm, Ho, Gd@NaYF$_4$ nanoparticles two different syntheses methodology were used. This optimized system composition and hierarchal nanostructure is intended to improve the upconversion emission of the Tm(III) and Ho(III) ions in the UV-VIS-NIR regions. The information about the crystalline phase, the morphology and the intensity of upconversion emission were obtained using: X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Luminescence Spectroscopy (LS). In the future, this system may be tested for bioimaging and phototherapy studies.

Key words: Lanthanides, luminescence, nanoparticles

Introduction
Lanthanide-doped nanoparticles are extensively studied nowadays and specifically in biological area they may be used as luminescent labels for imaging applications. Normally, these systems show upconversion emission that consists in absorption of low energy and the emission of higher energy photons. This phenomenon is interesting for biological media since these nanoparticles may absorb light around 800 to 1000 nm, within the transparency window of biologic tissues. Moreover, in order to optimize the upconversion emission of the Tm(III) and Ho(III) ions it is usual to synthesize core@shell nanosystems. This is important whereas the inorganic shell would protect the lanthanide ions on the surface from non-radiative decay, which results in a high intensity of upconversion emission. Furthermore, other factors such as crystalline phase and nanoparticles size distribution size also influence the intensity of the upconversion emission of lanthanide ions. Aiming a possible application in luminescent imaging systems, this work intended to prepare core@shell NaYbF$_4$:Tm:Ho:Gd@NaYF$_4$ nanoparticles.

Results and Discussion
The precursors used in synthesis were the lanthanide trifluoroacetate (Ln(OC$_3$F$_3$)$_3$) and sodium trifluoroacetate (NaO$_2$C$_3$F$_3$) as source of fluoride and sodium ions, respectively. 1-octadecene, oleic acid and oleylamine are the solvent mixture and stabilizers. Two different synthetic methodologies were explored, using the same reagents. The mainly difference between them is the number of synthesis steps. In one of them, the reaction happens in one step where all the reagents are added in a specific sequential order resulting in core@shell system. On the other one, the core is prepared in the first step and it is added as a seed in the second step in the presence of the shell precursors. In order to induce the hexagonal crystalline phase an excess of sodium trifluoroacetate is added in the core synthesis in both methods, and this is a very important achievement about the methodology. The X-Ray Diffraction (XRD) data shows that the nanoparticles synthesized by both methodologies resulted in pure hexagonal phase for core-only and core@shell systems. The Transmission Electron Microscopy (TEM) shows that both methodologies lead to uniform particle morphology and a narrow particle size distribution. These results suggest that the methodologies were improved compared to previous developed projects. The upconversion emission spectra (UC-LS) of core@shell nanoparticles show higher intensity than the core-only nanoparticles suggesting the shell formation protected the Ln(III) ions from non-radiative decay. The upconversion emission spectra show bands attributed to electronic transitions characteristics of the Tm(III), Ho(III) and Gd(III) ions being promising for the suggested applications.

Conclusions
The results indicate that the methodology synthesis has been improved. The next step is to study the loading of photosensitizer molecules at the nanoparticles surface for photodynamic therapy. After this the NaYbF$_4$:Tm:Ho:Gd@NaYF$_4$ system may be tested for both imaging and phototherapy studies.

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