Synthesis and study of luminescent properties of NaYbF$_4$:Tm:Ho:Gd@NaYF$_4$ nanoparticles

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Abstract

In this work a photophysical study on NaYbF$_4$:Tm:Ho:Gd@NaYF$_4$ core@shell system was carried out. Two different synthetic methodologies were used in order to prepare NaYbF$_4$:Tm:Ho:Gd@NaYF$_4$ nanoparticles, intending to optimize the upconversion emission of the Tm(III) ion in the UV spectral region. 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), Luminescence Spectroscopy (LS).

Key words: lanthanides, luminescence, nanoparticles.

Introduction

Lanthanide ions-doped nanoparticles are very studied. Specifically in the biological area they may be used as luminescent labels for imaging applications. Normally, these systems present upconversion emission that consists in absorption of low energy and the emission of higher energy photons. That is interesting for biological media since they show low absorption of light around 850 to 1000 nm. Moreover, intending to optimize the upconversion emission of Tm(III) ions spectral region 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 nanoparticle distribution sizes also influence the intensity of the upconversion emission of lanthanide ions. Aiming a possible application in luminescent imaging systems and an efficient upconversion emission of the Tm(III) ion, this work intended to prepare core@shell NaYbF$_4$:Tm:Ho:Gd@NaYF$_4$ nanoparticles.

Results and Discussion

In this work lanthanide chlorides (LnCl$_3$) were used as precursors, oleic acid and 1-octadecene as stabilizers and ammonium fluoride (NH$_4$F) and sodium hydroxide (NaOH) as sources of fluoride and sodium ions, respectively. 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 in second vessel in the presence of the shell precursors. The X-Ray Diffraction (XRD) data shows the crystalline phase of the nanoparticles. The first methodology results in a pure hexagonal phase. On the other hand, the second methodology results in a core with a pure hexagonal phase and a core@shell system with a mixture of the hexagonal and cubic crystalline phases. The Transmission Electron Microscopy (TEM) shows that both methodologies lead to a non-uniform particle morphologies and size distribution. The results suggest that the methodologies must be improved in order to prepare monodisperse spheroidal core@shell nanoparticles with hexagonal crystalline phase required for high intensity of upconversion emission. The upconversion emission spectra (UC-LS) of core@shell nanoparticles show higher intensity than the core-only nanoparticles suggesting the shell formation. 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 application.

Conclusions

The results obtained indicate that one-step reaction methodology may be improved in order to prepare monodisperse spheroidal core@shell nanoparticles with hexagonal crystalline phase required for high intensity of upconversion emission.

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