Influence of chemical composition on the dissolution of AYF_4:Yb,Tm (A = Na, K or Li) upconverting nanoparticles in water

Darja Lisjak[1], Olivija Plohl[1,2], Boris Majaron[1], Maja Ponikvar-Svet[1]

[1] Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
darja.lisjak@ijs.si
[2] Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia

Abstract

Lanthanide-doped fluoride nanoparticles, which exhibit upconversion (UC) fluorescence have a great potential for biomaging and also as components in nanotheranostics.The UC process is characterized by the emission of light with shorter wavelength than that of the excitation source. Of particular interest for bioimaging is the UC at near infrared (NIR) wavelengths, so-called NIR-to-NIR UC, which is characteristic for the NPs co-doped with Yb^{3+} and Tm^{3+} [1]. Ternary fluorides, like for example $NaYF_4$, were proven to be one of the most suitable host matrices, which allow for efficient NIR-to-NIR UC.

Despite the known chemical stability of bulk fluorides (i.e., low solubility in water) [2] our preliminary study [3] revealed that $NaYF_4$:Yb^{3+},Tm^{3+} NPs can partly dissolve in water. This is not encouraging for biomedical applications, since lanthanide and flouride ions are cytotoxic in sufficiently large concentrations [4-6]. The aim of this work was to study the effect of chemical composition of ternary alkali fluoride NPs (AYF_4, where A = Li, Na or K) on the dissolution degree.

The AYF_4 NPs co-doped with Yb^{3+} and Tm^{3+} (Ln-NPs) were synthesized solvothermally at 200 °C. The synthesis time was adjusted in such a way that the Ln-NPs sizes were several tenths of nanometers. This was inspected with transmission electron microscopy while their crystal structures were analyzed with X-ray powder diffraction. The NIR UC emission of the Ln-NPs around 800 nm was much more intense than the blue emission at 450-470 nm. Aqueous suspensions with 1 mg/ml of Ln-NPs were aged from 1h and up to 3 days at room temperature and at pH ~ 7.4 (similar to that of blood). The solutions, which were obtained after ultrafiltration of the Ln-NPs, were analyzed for the dissolved F^- and cations using a combined fluoride ion selective electrode and optical emission spectroscopy, respectively. Partial dissolution of all the studied Ln-NPs was confirmed and will be discussed in terms of their composition.

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