Tuning Metal-enhanced Up-conversion in Single Core-shell $NaYF_4:Er^{3+}/Yb^{3+}$ Nanocrystals Coupled to Silver Nanowires

M. Ćwierzona[1], A. Prymaczek[1], A. Bednarkiewicz[2], S. Maćkowski[1] D. Piątkowski[1],

[1]Institute of Physics, Department of Physics, Astronomy and Informatics,
Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
[2]Institute of Low Temperature and Structure Research,
Polish Academy of Science, Okolna 2, 50-422 Wroclaw, Poland
E-mail: dapi@fizyka.umk.pl

In recent years, up-converting materials, in particular rare-earths doped $NaYF_4$ nanocrystals (NCs) have attracted considerable interest. Due to optical stability, low toxicity, and high signal-to-noise ratio of the up-conversion emission, they can be used for designing new bio-medical markers [1], infrared sensitizers [2] or optoelectronics devices [3]. However, commercial applications are somewhat limited due to relatively low efficiency of the up-conversion process. One of the approaches to overcome this issue is Metal Enhanced Fluorescence (MEF), an effect associated with placing emitters in the vicinity of metallic nanoparticles.

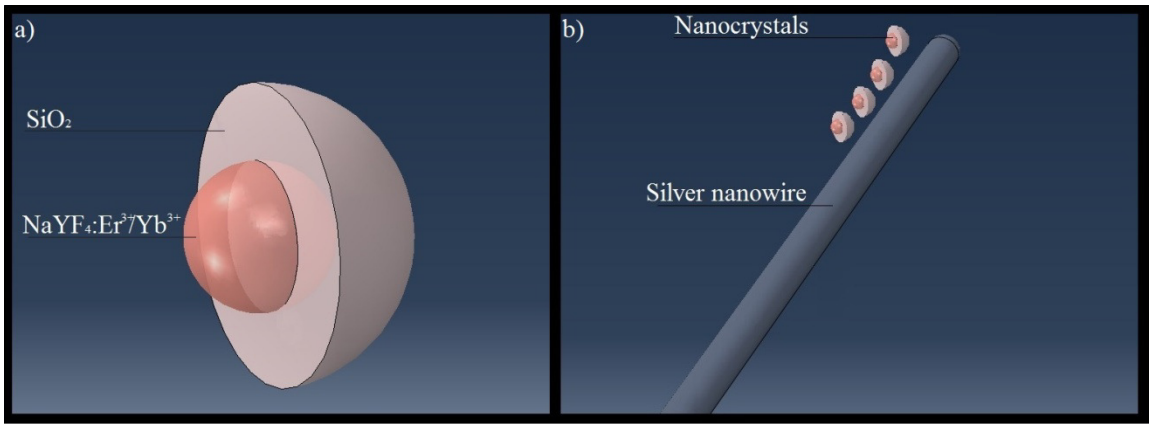

Figure 1. $NaYF_4:Er^{3+}/Yb^{3+}$ NCs coated by SiO_2 (a) and coupled to single silver nanowires (b)

In this work, we describe the optical properties of hybrid nanostructures that consist of Er^{3+}/Yb^{3+} doped $NaYF_4$ nanocrystals coupled to single silver nanowires (NWs). In order to optimize the MEF effect, observed previously for such nanostructures [4], NCs were coated by optically passive SiO_2 shells with thicknesses up to 9 nm (Fig. 1). Core of the $NaYF4:Er^{3+}/Yb^{3+}$ nanocrystals was the same and equal to approximately 20 nm in diameter. In the experiment we used scanning confocal fluorescence microscope (Nikon Ti-S), equipped with piezo-electrically controlled sample holder and high NA oil-immersion objective (Nikon 60x NA=1.4). For excitation we used 980 nm CW/pulsed fiber-coupled laser diode. The emission signal was filtered by band pass filters (550 and 650 nm), matched to the Er^{3+} emission lines.

Luminescence was detected by APD (Perkin Elmer, SPCM-AQR-14), coupled to a counter. For time-resolved experiments we used multiscaler card (Becker&Hickl, MSA-300) and programmable generator synchronizing the setup.

First, we studied the optical properties of individual nanocrystals deposited on a glass surface, for the sake to acquire reference data. We noticed significant increase of the luminescence intensity with increasing thicknesses of the silica shell. Namely, in the case of red luminescence (650 nm) the intensity increases – on average – from 15 kcps up to 40 kcps. The increase of emission intensity was accompanied by lengthening of the luminescence decay times, respectively, from 220 µs up to 351 µs. This effect, observed for both emission lines, can be explained by insulating properties of the silica shell, as by increasing the SiO_2 thickness we minimize any negative impact (quenching) of the oleic acid that is used as stabilizer during the synthesis. Next, we focus on elucidating the effect of the silica shell on the interaction between NCs and metallic nanoparticles. Thus, we coupled the NCs to single Ag NWs. Importantly, all types of NCs exhibit substantial enhancement (around factor of 5-6) upon coupling with plasmon excitations in silver nanowires. Again, this effect is demonstrated at the single nanocrystal level. Furthermore, this increase of emission intensity walks along the shortening of the emission decay times, which proves that coupling to silver nanowires can tune the emission rates of the NCs.

We conclude that increase of the SiO_2 shell thickness positively influences the luminescence properties of $NaYF_4:Er^{3+}/Yb^{3+}$ nanocrystals. The silica shell reduces surface-quenching, and, despite increasing the distance to the nanowire, does not diminish the benefits of coupling to metallic nanoparticles.

Funding: National Science Centre of Poland, projects: 2013/09/D/ST3/03746 and 2013/10/E/ST3/00034

References:

[1] Z. S. Haidar, *Bio-Inspired/-Functional Colloidal Core-Shell Polymeric-Based NanoSystems: Technology Promise in Tissue Engineering, Bioimaging and NanoMedicine.* Polymers 2010, **2**, 323–352

[2] J. Grzelak, K. Ciszak, M. Nyk, S. Mackowski, D. Piatkowski, *Extending light-harvesting of poly(3-hexylthiophene) through efficient energy transfer from infra-red absorbing nanocrystals: Single nanoparticle study*, Appl. Phys. Lett. 2014, **105**(16) 163114

[3] D. Zhang, C. Chen, F. Wang , D.M. Zhang, *Optical Gain and Upconversion Luminescence in LaF3: Er, Yb Nanoparticles-Doped Organic–inorganic Hybrid Materials Waveguide Amplifier*. Appl. Phys. B 2009, **98**, 791–795

[4] D. Piatkowski, N. Hartmann, T. Mancabelli, M. Nyk, S. Mackowski, and A. Hartschuh, *Silver nanowires as receiving-radiating nanoantennas in plasmon-enhanced up-conversion processes,* Nanoscale 2014, **7**(4), 1479–1484