Understanding Plasmon Enhanced Up-Conversion in Single Nanocrystals using Polarization-resolved Fluorescence Lifetime Imaging Microscopy

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

[1]*Institute of Physics, Department of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

[2]*Advanced Materials Engineering and Modelling Group, Faculty of Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland*

E-mail: mackowski@fizyka.umk.pl

Metal Enhanced Fluorescence (MEF) is one of the key processes observed at the nanoscale [1]. It has been demonstrated that coupling metallic nanoparticles (i.e. spheres, cubes, rods, wires) to single emitters (i.e. dyes, proteins, chlorophylls, quantum dots, nanocrystals) can modify the absorption and/or emission rates, improve photostability or introduce sensitivity to polarized light [2-5]. Interactions that take place between single emitters and elongated metallic nanoparticles (i.e. silver nanowires) can often lead to puzzling results, in particular when polarized light is used for excitations. Including Surface Plasmon Polaritons (SPPs) that can freely propagate for quite long distances in metallic nanostructure, additionally blur any sharp distinction between enhancement of absorption and emission, as well as their overall contribution to the MEF.

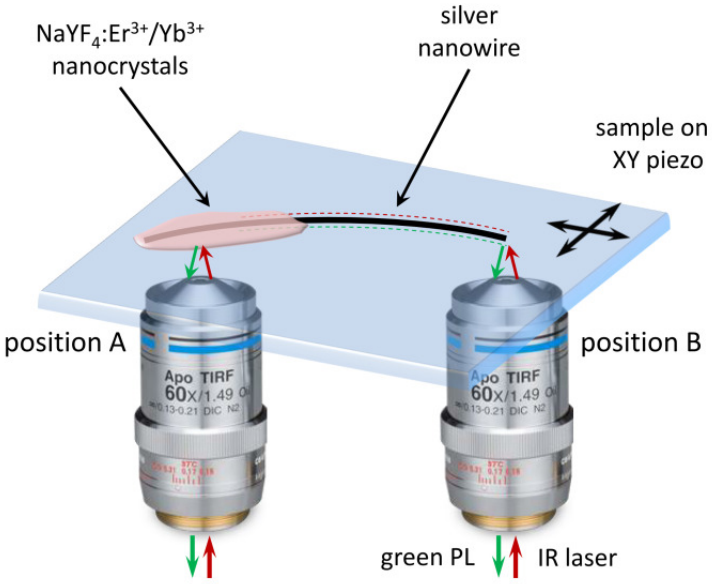

Fig. 1. General concept of the experiment. Nanocrystals localized in the vicinity of silver nanowire can be excited directly (position A) or through SPPs started at the other end of Ag nanowire (position B).

In this work we develop a polarization-resolved Fluorescence Lifetime Imaging Microscopy (FLIM) technique for up-converting nanocrystals and demonstrate the applicability of this approach to disentangle various contributions to the overall MEF. We studied $NaYF_4$ nanocrystals (NCs) doped with Er^{3+} ions, that were coupled to single silver nanowires (NWs). The sample was prepared in such a way that only one third of the length of the nanowire was covered by NCs (Fig. 1). Thereby, NCs could be excited either directly by a focused laser beam (position A) or indirectly through propagating SPPs launched on the opposite end of the NW (position B), where no NCs are located. In order to ensure spectral separation between excitation and emission wavelengths, we applied IR excitation (980 nm) of the NCs, that activates up-conversion luminescence at 550 nm and 650 nm.

First, we directly excited NCs coupled to the silver NW (position A) with linearly polarized light. Polarization vector (after high NA objective) was perpendicular to the nanowire, but its orientation could be switched between vertical (V) and horizontal (H) orientation relative to the substrate. Acquired photoluminescence (PL) intensity maps show significant increase of the NCs emission intensity (placed close to the NW) for both laser polarizations. Nevertheless, only for H polarization we observed significantly shortened PL decay time (increased emission rate), what we attribute to the metal enhanced emission. For V laser polarization interaction between NCs and NW is much more weaker, thus plasmon enhanced/mediated absorption dominates the process. Indeed, only V polarized light can efficiently launch propagating plasmons, what has been tested by focusing laser spot directly on silver nanowire (position B). The experimental results can be verified by theoretical calculations.

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

References:

[1] L. Novotny and B. Hecht, Principles of Nano-Optics. Cambridge University Press, 2006.
[2] J. R. Lakowicz, Anal. Biochem., vol. 337, no. 2, pp. 171–194, 2005.
[3] S. Mackowski, J. Phys. Condens. Matter, vol. 22, no. 19, p. 193102, 2010.
[4] N. Mauser, D. Piatkowski, T. Mancabelli, M. Nyk, S. Mackowski, and A. Hartschuh, ACS Nano, vol. 9, no. 4, pp. 3617–3626, 2015.
[5] D. Piatkowski, N. Hartmann, T. Macabelli, M. Nyk, S. Mackowski, and A. Hartschuh, Nanoscale, vol. 7, no. 4, pp. 1479–1484, 2015.