Distance dependent graphene-rare-earths energy transfer in core-shell up-conversion nanocrystals

Aneta Prymaczek
M. Ćwierzona¹, D. Piątkowski¹, A. Bednarkiewicz²
S. Maćkowski¹

¹Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland
² Institute of Low Temperature and Structure Research, PAS, Okólna 2, 50-422 Wrocław, Poland
anetap@doctorant.umk.pl

We present spectroscopic properties of rare-earths (Er³⁺/Yb³⁺) doped NaYF₄ up-conversion nanocrystals (NCs), coupled to a graphene layer. Graphene incorporated in hybrid assemblies containing up-converting NCs holds promise for designing new biosensing and photovoltaic devices [1, 2]. Non-radiative energy transfer that takes place between NCs and graphene, is a key problem for graphene-based platforms and has been studied in this work.

Nonradiative energy transfer from an emitter to graphene layer depends both on the emission wavelength and on the number of graphene layers [3]. In this work, however, we demonstrate how distance between NCs and graphene influences efficiency of energy transfer. For this reason, investigated NCs has been covered with silica shell with a thickness ranging from 0 to 11 nm.

In the experiment we examined single NaYF₄:Er³⁺/Yb³⁺ NCs deposited on graphene using fluorescence microscopy. The same nanocrystals deposited on glass served as reference. The samples were investigated with a confocal fluorescence microscope (Nikon, Ti-S) and illuminated through an oil-immersion, high numerical aperture objective (Nikon 60x NA=1.4). For excitation we used CW/pulsed laser diode, operating at the 980 nm. The Er³⁺ doped NCs show two distinct up-conversion emission lines, centered at 540 nm and 650 nm.

First of all, NCs on glass characterize increase of the luminescence intensity and luminescence decay times with increasing shell thickness, observed for both emission lines. This is due to reduced interaction with surface ligands [4]. The same NCs coupled to graphene feature additional change of the luminescence kinetics. Emission decay times distinctly decrease with decreasing shell thickness. For shell 7-11 nm we noticed shortening of the luminescence decay times from 290 µs to 180 µs, for shell 4-7 nm from 260 µs to 130 µs, and from 190 µs to 110 µs for NCs without shell (concerns red emission). At the same time, we observed noticeable decrease of the NCs emission intensity. In general, we observed decrease of about 20%, with respect to the reference.

Our results show that in NCs-graphene platform non-radiative energy transfer from NCs to graphene is very sensitive to distance variations. Relatively weakly affected intensity of the emission allows further development of such a NCs-graphene platform.

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References