PHD PROJECT DESCRIPTION
(4000 characters max., including the aims and work plan to de published online)

Mechanisms of Plasmon-Enhanced Up-Conversion: Controlling Excitation, Energy Migration, and Emission at the Single-Nanocrystal Level

1.1. Project goals

The aim of the project is the experimental identification of mechanisms governing photon up-conversion in single nanocrystals in the presence of plasmonic near-fields generated by metallic nanoparticles. We hypothesize that plasmonic near-fields enable selective control over excitation pathways and energy redistribution, leading to distinct regimes where either excitation or emission processes dominate the optical response. A comprehensive understanding of each of these stages will enable the design of nanocrystals with enhanced efficiency and functionality.

The following specific objectives will be pursued within the project:

- to identify the role of plasmonic near-fields generated by metallic nanoparticles in excitation and energy migration processes, in particular to determine the extent to which local and anisotropic near-fields influence the spatial distribution and dynamics of excited-state ion populations within the nanocrystal volume,
- to determine the mechanisms of emission coupling to plasmonic nanostructures, with particular emphasis on the conditions leading to emission enhancement or quenching, as well as the role of plasmonic radiative channels,
- to develop criteria enabling control and optimization of the optical response of the system by tuning the contributions of excitation and emission processes, including the identification of conditions governing transitions between these regimes.

1.2. Outline

Photon up-conversion in rare-earth-doped nanocrystals is a nonlinear optical process involving the conversion of lower-energy (infrared) photons into higher-energy photons (visible). This phenomenon finds applications, among others, in biomedical imaging and nanoscale optical sensing. However, despite its growing application potential, the conversion efficiency remains limited. Although it has been shown that coupling nanocrystals with plasmonic nanostructures can lead to a significant enhancement of the optical response, the physical mechanisms responsible for this effect remain unclear.

In particular, it remains unclear under which conditions the observed optical response is governed by changes in excitation processes, by energy redistribution within the nanocrystal, or by modifications of emission pathways associated with coupling to plasmonic radiative modes. Therefore, a key challenge is to unambiguously disentangle these contributions.

The central idea of the project is to exploit plasmonic near-fields as active research tools. Owing to their strong spatial localization around metallic nanoparticles (tens of nanometers), it becomes possible to selectively excite different regions of a nearby nanocrystal, leading to the formation of spatially and temporally heterogeneous populations of excited ions, whose relaxation and energy redistribution can be probed spectroscopically. This understanding is essential for the rational design of nanoscale optical probes and sensing platforms.

To access different regimes of these processes, two complementary physical systems will be employed. The first consists of nanocrystals doped with Tm^{3+} ions, operating in the unique photon avalanche regime, characterized by a slow build-up of the excited-state population (ms) and pronounced energy migration, enabling direct tracking of excitation dynamics and energy redistribution within the volume of an anisotropically excited nanocrystal. The second system comprises Er^{3+}/Yb^{3+} co-doped nanocrystals, exhibiting relatively fast energy transfer and conversion dynamics (μs), which allows investigation of emission mechanisms and coupling to plasmonic modes. The combination of these two systems will provide a coherent picture of energy flow and conversion in nanocrystals coupled to plasmonic nanostructures.

The uniqueness of the project lies in the combination of advanced synthesis methods for up-conversion nanocrystals with state-of-the-art experimental techniques enabling studies at the single-nanoobject level. The experiments will be carried out using anti-Stokes confocal microscopy, incorporating, among others, high-resolution and high-sensitivity imaging, time-resolved techniques, and Fourier-plane imaging. The project will be further supported by collaboration with specialized research groups, providing access to complementary expertise in nanomaterial synthesis and electromagnetic simulations.

1.3. Work plan

I. In the first stage, up-conversion nanocrystals doped with Tm^{3+} and Er^{3+}/Yb^{3+} ions will be synthesized, preliminarily characterized, and subsequently integrated with plasmonic nanostructures featuring controlled geometry and emitter-metal separation. The work will be carried out in collaboration with research groups specializing in nanomaterial synthesis (Prof. A. Bednarkiewicz, INTiBS PAS, Wrocław), design and modeling (Prof. K. Słowik, NCU, Toruń), as well as fabrication of plasmonic nanoparticles (Prof. J. Niedziółka-Jönsson, IChF PAS, Warsaw) and plasmonic substrates (Prof. A. Bouhelier, CNRS, Dijon) with tailored properties.

II. The second stage will focus on advanced optical characterization of single nanocrystals using single-molecule anti-Stokes microscopy combined with spectrally and time-resolved measurements. In particular, advanced luminescence imaging techniques, fluorescence lifetime imaging microscopy (FLIM), and back focal plane (BFP) analysis will be employed to probe excitation dynamics, energy migration, and emission pathways. In addition, polarization-dependent up-conversion efficiency measurements will be performed to control and analyze the coupling conditions between emitters and plasmonic near-fields (in collaboration with Prof. A. Hartschuh, LMU, Munich).

III. In the final stage, the obtained results will be subjected to quantitative analysis and interpreted using kinetic modeling of excitation dynamics and radiative processes. This will enable identification of the dominant physical mechanisms and determination of the conditions under which excitation and emission processes govern the optical response of the investigated systems.

1.4. Literature (max. 7 listed as a suggestion for a PhD candidate preliminary study)

[1] F. Auzel, *Upconversion and Anti-Stokes Processes with f and d Ions in Solids*, Chem. Rev. 104, 1 (2004).
[2] P. Bharadwaj, P. Anger, and L. Novotny, *Nanoplasmonic enhancement of single-molecule fluorescence*, Nanotechnology 18, 4 (2007).
[3] D. Piatkowski, N. Hartmann, T. Macabelli, M. Nyk, S. Mackowski, and A. Hartschuh, *Silver nanowires as receiving-radiating nanoantennas in plasmon-enhanced up-conversion processes*, Nanoscale 7, 4 (2015).
[4] N. Hartmann, D. Piatkowski, R. Ciesielski, S. Mackowski, and A. Hartschuh, *Radiation Channels Close to a Plasmonic Nanowire Visualized by Back Focal Plane Imaging*, ACS Nano 7, 11 (2013).
[5] M. Dudek, M. Szalkowski, M. Misiak, M. Ćwierzona, A. Skripka, Z. Korczak, D. Piątkowski, P. Woźniak, R. Lisiecki, P. Goldner, S. Maćkowski, E. M Chan, P.J. Schuck, A. Bednarkiewicz, *Size-Dependent Photon Avalanching in* Tm^{3+} *Doped* $LiYF_4$ *Nano, Micro, and Bulk Crystals*, Adv. Opt. Mater. 10, 2201052 (2022).
[6] S. Wen, J. Zhou, K. Zheng, A. Bednarkiewicz, X. Liu, and D. Jin, *Advances in highly doped upconversion nanoparticles*, Nat. Commun. 9, 2415 (2018).

1.5. Required initial knowledge and skills of the PhD candidate

- solid knowledge of physics fundamentals, in particular optics, optical spectroscopy, and solid-state physics,
- basic experience in experimental work, preferably in an optical, spectroscopic, or microscopy laboratory,
- interest in nanotechnology, optical technologies, and electronics,
- basic skills in data analysis and programming (e.g., MATLAB, Mathematica, LabVIEW, Python),
- high level of motivation, persistence, and a systematic approach to research,
- good command of English enabling independent analysis of scientific literature and effective presentation of results.

1.6. Expected development of the PhD candidate's knowledge and skills

- in-depth understanding of the physics of modern nanomaterials, with particular emphasis on light–matter interactions at the nanoscale,
- knowledge of advanced optical microscopy and spectroscopy techniques for nanostructures,
- experience in the design and implementation of modern physical experiments,
- skills in the analysis, interpretation, and presentation of experimental data,
- fundamental knowledge of physical process modeling and integration of models with experimental data,
- scientific writing and dissemination skills (publications and conference presentations).