Excitation pathways in upconverting nanoparticles in the vicinity of silver nanowires

A. Borodziuk[1], K. Sulowska[2], Ł. Zinkiewicz[3], M. Szymura[1], A. Reszka[1], A. Bogucki[3], B. Sikora[1], S. Maćkowski[2], Ł. Kłopotowski[1]

[1] Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
[2] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, 87-100 Toruń, Poland
[3] Institute of Experimental Physics, Faculty of Physics, University of Warsaw, 02-093 Warsaw, Poland

Motivation

Plasmonic nanostructures are commonly used to enhance the upconverting luminescence (UCL) of β-$NaYF_4$:Er^{3+},Yb^{3+} (UCNPs). In our work, we would like to determine how the presence of silver nanowires (AgNW) affects UCL. To this end, we conducted the experiments in high power excitation regime using AgNW-UCNPs nanohybrids. This allows us to answer the following question: is AgNWs impact to excitation, energy transfer or emission efficiency of UCNPs?

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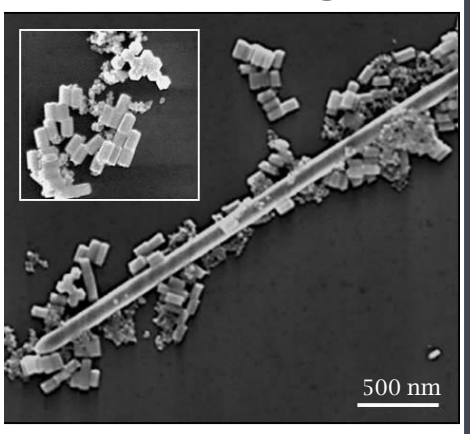
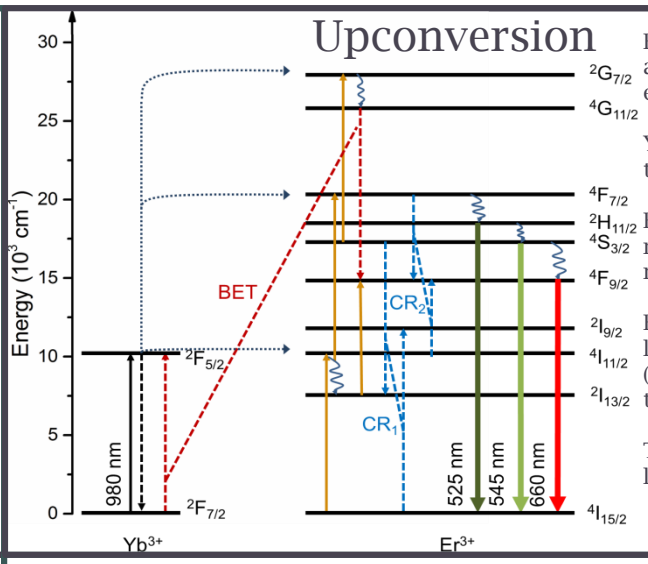
Morphology



SEM image of AgNW-UCNPs nanohybrid.

Upconversion



Black thin/dashed arrow – excitation/deexcitation.

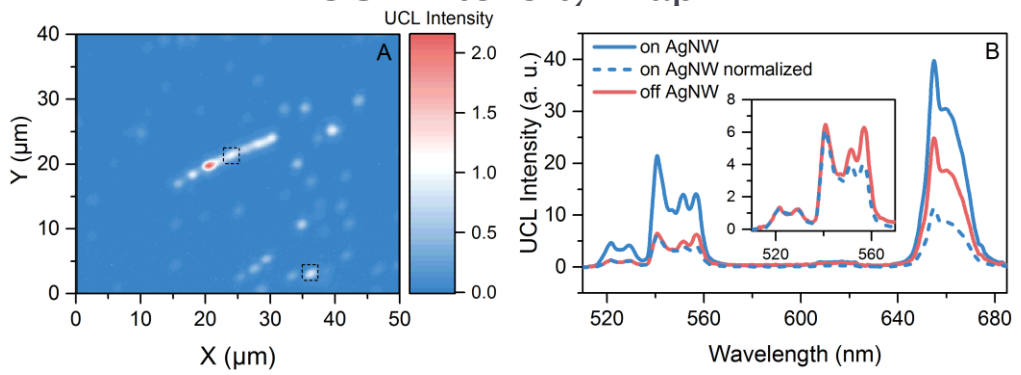
Yellow arrows – energy transfers.

Blue wavy lines – multiphonon energy relaxation.

Blue and red dashed lines – cross-relaxation (CR) and back energy transfer (BET)

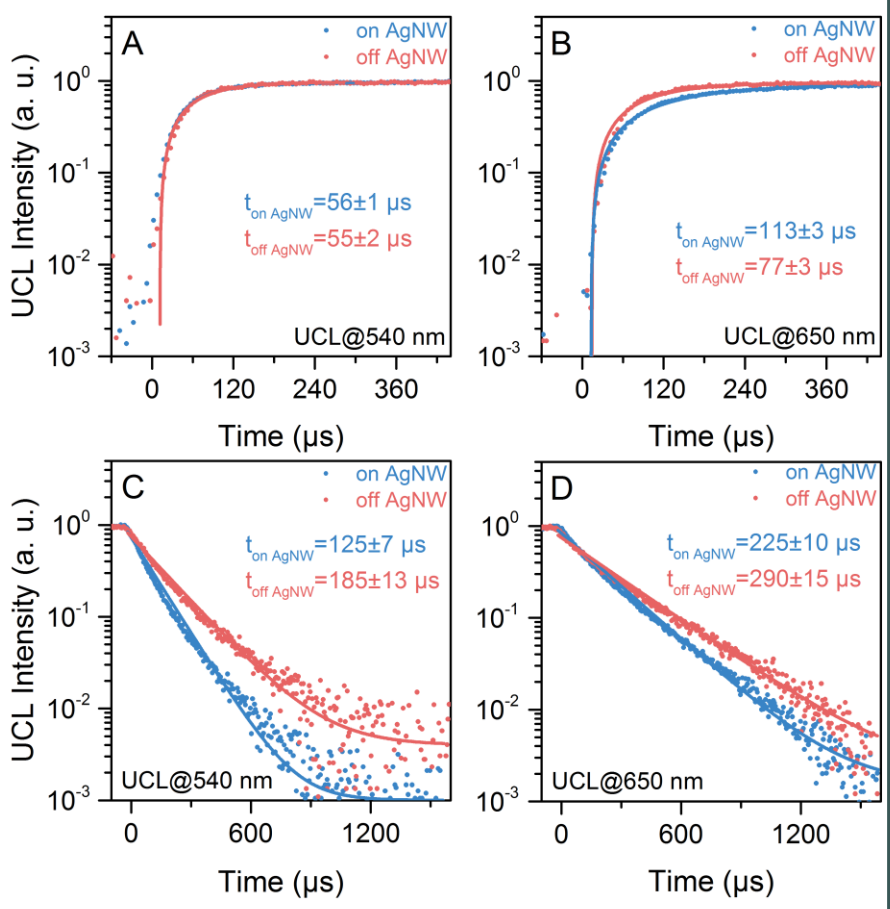
Thick green and red lines – light emission.

UCL intensity map



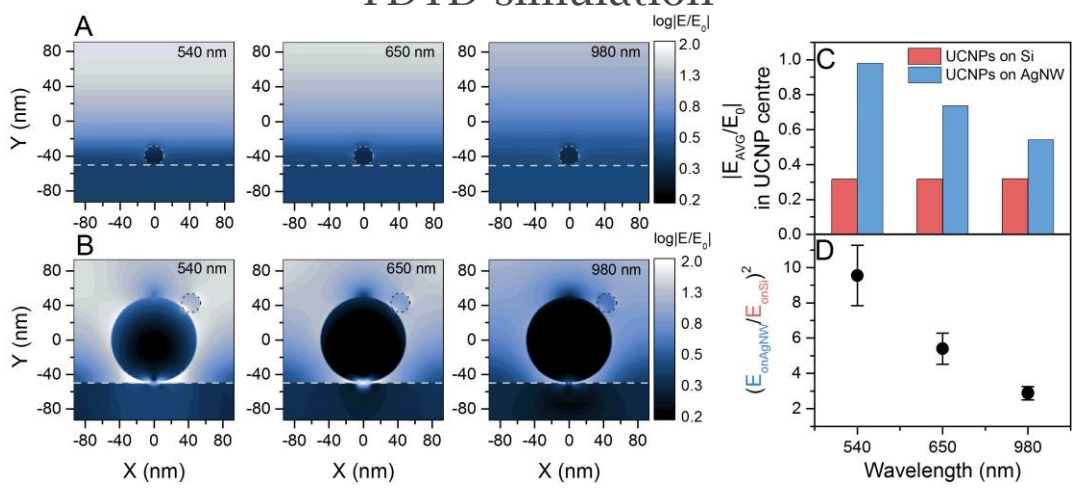
UCL intensity map of the emission from the UCNPs adsorbed on the AgNW surface and uncoupled ones. Black dashed squares outline the area from which the UCL decays were collected. (B): UCL spectra extracted from the map in (A) for the UCNPs on (blue) and off (red) the AgNW. The dashed blue line is the UCL spectrum for the UCNPs on the AgNW normalized at the two-photon green band at 540 nm.

UCL dynamics



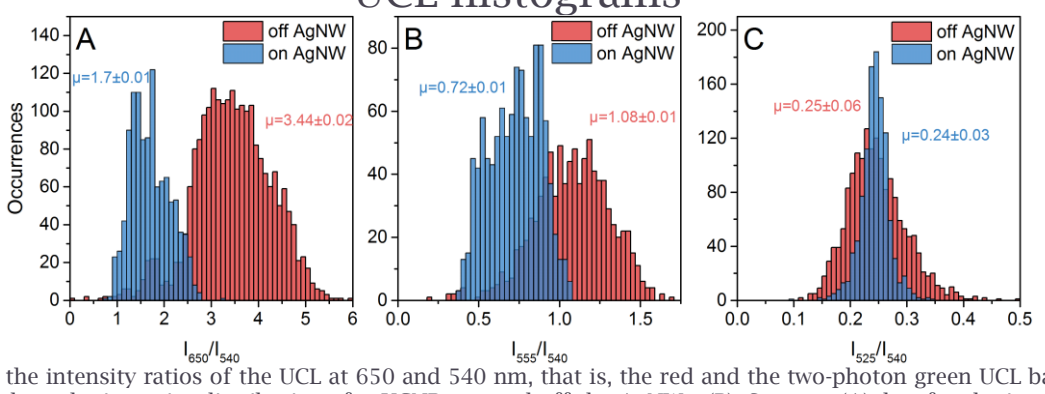
(A, B): Rise dynamics of the green and red bands UCL, respectively. Points are experimental data, lines are fits of the monoexponential rise: $I(t)=A(1-\exp(-t/\tau_r)$, where A is an amplitude, τ_r is the rise time. (C, D): Decay dynamics of the green and red UCL bands, respectively. Points are experimental data, lines are fits of the monoexponential decay: $I(t) = A \exp(-t/\tau_d) + I_0$, where A is an amplitude, τ_d is the decay time, and I_0 is the background level. The rise and decay time traces were shifted so that t = 0 corresponds to the moment of switching on and off the laser, respectively.

FDTD simulation



Electric field distributions simulated with FDTD method for an UCNP at a Si substrate (A) and for an UCNP interfaced with a AgNW on a Si surface (B), for three indicated wavelengths. The Si/vacuum interface is at Y = −50 nm. (C): Comparison of the electric field amplitudes simulated at the UCNP center for UCNPs on the AgNW (blue bars) and on the Si substrate (red bars). (D): Simulated electric intensity enhancement due to the presence of AgNW, averaged over the position of the UCNP along the wire perimeter.

UCL histograms



Distributions of the intensity ratios of the UCL at 650 and 540 nm, that is, the red and the two-photon green UCL bands. Blue and red histograms show the intensity distributions for UCNPs on and off the AgNWs. (B): Same as (A), but for the intensity ratios of the UCL at 555 and 540 nm, that is, the three-photon and the two-photon green UCL bands. (C): Same as (A), but for the temperature-dependent intensity ratios of the UCL at 525 and 540 nm, that is, the two two-photon green UCL bands.

Conclusions

- The results presented in this work revealed that the interaction between UCNPs and AgNWs cause modification of the luminescence spectrum.
- The decay luminescence measurements indicated that it is caused by an enhanced decay rate of $^4S_{3/2}$ state in Er^{3+} ions. Therefore, the efficiency of the three-photon excitation mechanism decreased.
- Moreover, hyperspectral mapping technique reveals negligible excitation-induced heating of UCNPs, neither directly nor by the nanowire plasmons.

E-mail: aborodziuk@ifpan.edu.pl