Investigation of surface quenching effect in ultra-small upconverting nanoparticles

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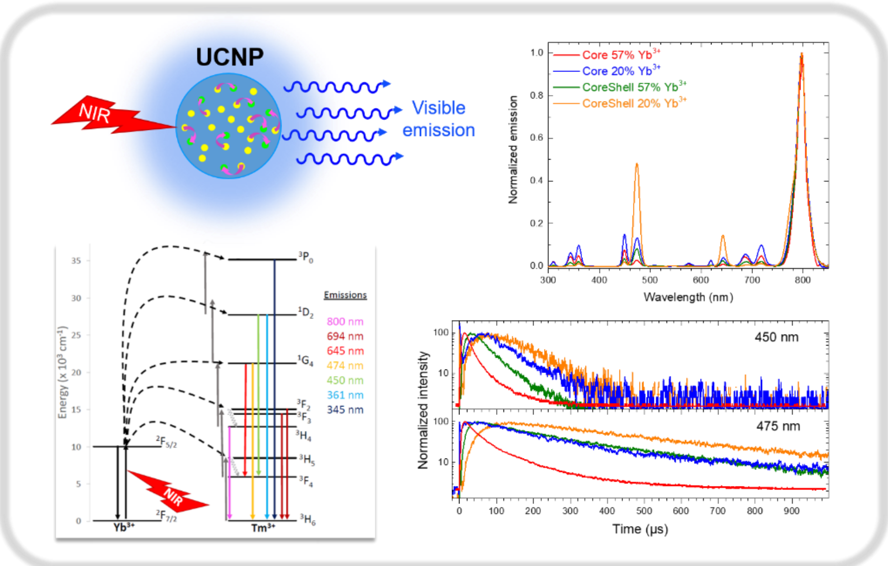
Reducing the size of upconverting nanoparticles down to less than 5 nm is appealing for nano-imaging applications. Based on a microwave heating cycling process, it is now possible to get emissive β-crystal phase particles of about 3 nm. For such ultrasmall particles, the effect of surface quenching on their photophysical properties is a key issue that needs to be mastered to optimize their emissivity. At the same time, understanding the surface effect on the discrete emissions of UCNPs is not trivial. Therefore, we investigate here the influence of the presence of an inert 1 nm-thick $NaGdF_4$ shell as well as the composition of the core (%Yb^{3+}) on the photophysical properties of ultrasmall Tm^{3+}-based particles (core of 3.5 nm diameter) using steady state and time-resolved spectroscopy. Steady-state band intensity ratios are confronted to variations of the average lifetimes of the emission decays for the corresponding transitions and will be discussed in terms of surface quenching effects related to the composition of the core in order to understand the mechanisms of the energy transfers occurring in these sophisticated nanoparticles.



Figures: A. Schematic view of an upconverting nanoparticle (UCNP). B. Dieke diagram of a Yb^{3+},Tm^{3+}-doped UCNP showing energy levels of the Yb^{3+} sensitizer and Tm^{3+} emitter and energy transfers. C. Steady state emission spectra of ultra-small Tm^{3+}-based UCNPs varying by the presence/absence of a shell and by their doping in Yb^{3+} ions. D. Time-resolved emissions at 450 and 475 nm of core particles with 57 % (red) and 20% Yb^{3+} (blue), and core-shell particles with 57 % (green) and 20% Yb^{3+} (orange).