

Quenching pathways in NaYF₄:Er³⁺,Yb³⁺ upconversion nanocrystals

Upconversion materials are unconventional color-conversion materials that can absorb low-energy and emit higher-energy photons. Of particular interest have been β -NaREF₄ nanocrystals (NCs; with RE = Y, Gd, or Lu) doped with either Er³⁺ or Tm³⁺ and often co-doped with Yb³⁺ or other lanthanides to tune absorption strength or emission color. Such NCs exhibit narrow-line emissions, and they are photochemically and colloiddally stable, making them ideal for spectral conversion in next-generation photovoltaics or background-free biomedical imaging, but also for temperature sensing. Despite over 10 years of development, it has not been possible to synthesize nanocrystals (NCs) with upconversion efficiencies on a par with what can be achieved in bulk materials. To guide the design and realization of more efficient upconversion NCs, a better understanding of the loss pathways competing with upconversion is necessary.

Here, we study the excited-state dynamics of the workhorse upconversion material, β -NaYF₄ co-doped with Yb³⁺ and Er³⁺. For each of the energy levels involved in infrared-to-visible upconversion, we measure the competition between spontaneous emission, energy transfer between lanthanide ions, and other decay processes (Figure 1A). We present a microscopic model that can quantitatively predict the different quenching dynamics of bulk upconversion material, core-only NCs, and core-shell NCs (Figure 1B). An important quenching pathway for NCs is energy transfer to high-energy vibrations of solvent and/or ligand molecules on the surface, as evidenced by the effect of energy resonances between electronic transitions of the lanthanide ions and vibrations of the solvent molecules. However, the strongest contribution to reduced upconversion efficiencies in NCs comes from quenching of the near-infrared energy levels (Er³⁺: ⁴I_{11/2} and Yb³⁺: ²F_{5/2}), which is likely due to vibrational coupling to OH⁻ defects incorporated in the NCs during synthesis. Indeed, we find that new NC synthesis procedures that avoid the use of OH⁻-containing Na⁺-precursors, lead to significantly less quenching and efficiencies approaching the bulk materials, which we ascribe to lower OH⁻ defect concentrations.

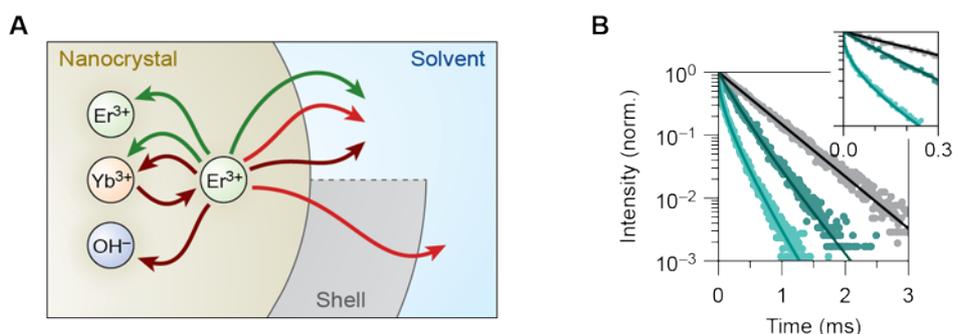


Figure 1 | Energy-transfer and quenching dynamics in NaYF₄:Er³⁺,Yb³⁺ upconversion nanocrystals. (A) Schematic: from any of the various energy levels involved in upconversion (⁴S_{3/2}, green; ⁴F_{9/2}, red; ⁴I_{11/2}, infrared), an Er³⁺ ion suffers losses due to energy transfer to neighboring lanthanide centers, OH⁻ defects, or organic molecules. (B) Example: the decay dynamics of the red ⁴F_{9/2} emission of Er³⁺ in bulk β -NaYF₄ (gray/black), core-shell NCs (dark green), and core-only NCs (lighter green). With a single fit parameter for solvent quenching, our microscopic model (solid lines) reproduces the experimental dynamics of the three samples (data points), including the strongly multi-exponential early-time signal (see inset).

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