Abstract

Among the many remarkable properties of upconverting nanoparticles (UCNPs), perhaps none is more compelling than their ability to shift the boundaries of imagination surrounding light-matter interactions. These nanomaterials—typically doped with trivalent lanthanide ions—are known for their capacity to sequentially absorb multiple low-energy photons, followed by the emission of a single photon of higher energy. The nonlinear character of this process, coupled with the long-lived intermediate states intrinsic to rare-earth ions, has made UCNPs indispensable across applications in microscopy, bioimaging, sensing, and photonics. And yet, despite the breadth of this field, key questions remain—not only about how to extract brighter signals, but how to exert finer control over emission itself.

This work began with a deceptively simple question:

Can light be used not just to drive emission, but to shape it?

This idea became the inspiration—*spiritus movens*—for exploring whether emission pathways could be controlled through **co-excitation**—two independent beams, each resonant with specific transitions, working *together* to sculpt emission in ways a single beam could not.

To pursue this, a dual-beam optical system was developed—featuring collinear excitation from a fixed 975 nm diode laser—resonant with transitions in ytterbium ions present alongside the emitting ions in these materials—and a tunable NIR beam spanning 1050-1875 nm, generated via difference-frequency generation. This system provided not only wavelength precision but also spectral and spatial stability, enabling the exploration of co-excitation across a wide range of conditions.

The journey through the winding pathways of photophysical properties began with thulium-doped nanoparticles, and along the way revealed effects that *exceeded all expectations*. Two spectral regions of the tunable NIR beam—centered around **1213** and **1732 nm**—emerged as particularly cooperative: a beam at each of these wavelengths, when used alone, produced negligible emission; yet when paired with 975 nm, they yielded dramatic enhancements in upconversion. In some cases, the resulting emission surpassed the additive contributions of both beams by **several hundred percent**—that is, their combination yielded *a much higher emission intensity* than the sum of the intensities produced by each beam alone.

A surplus metric was introduced to quantify this excess, and phenomenological models were proposed to describe its dependency on excitation power. Beyond this quantifiable surplus, the low-power regime revealed a more profound phenomenon: ***de novo*** emission—light produced only when both beams acted together, since neither could induce it alone.

To illustrate the implications of this finding, a 1732 nm beam—otherwise invisible to silicon detectors—was directly visualized through co-excitation with 975 nm. Using a microscope slide coated with upconverting nanoparticles as a phosphor and a standard photographic camera, this approach enabled real-time, switchable, and spatially resolved imaging of the beam profile, serving as a practical proof-of-concept for extending spectral conversion—in effect, bringing infrared radiation well beyond the reach of conventional detectors into view.

The study then turned to erbium-based systems, where cooperative behavior was also observed—though with a different texture. A beam at **1523 nm** produced measurable emission on its own, but only a modest surplus when paired with 975 nm. A second region, centered at **1139 nm**, yielded a much more compelling effect: the beam remained dormant in isolation, yet under co-excitation with the 975 nm beam it consistently gave rise to amplified emission. Since 1139 nm photons correspond strictly to excited-state absorption, this wavelength served as a model for co-excitation without ground-state absorption contributions.

Further studies using *only* the 1139 nm beam—without the 975 nm beam—at high power revealed unusual emission behavior that varied with erbium concentration. Sudden shifts in response, along with increased nonlinearity, pointed to feedback effects—perhaps even **energy looping**. While the exact mechanisms remain under investigation, it is already clear that this may be less of a conclusion and more of a prelude to something entirely new.

In the end, the story that began with a question of control leads to one lasting idea: co-excitation is more than just a way to enhance emission—it is a subtle yet powerful tool for shaping it.