

# Bioimaging and Nanothermometry using Multi-Photon Excited Nanoparticles: Towards a Multi-Modal Nanoplatform

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Multi-photon excited luminescent nanomaterials such as semiconductor quantum dots (QDs) or gold nanorods (GNRs) are emerging as useful tools in diagnostic medicine and therapeutics. These

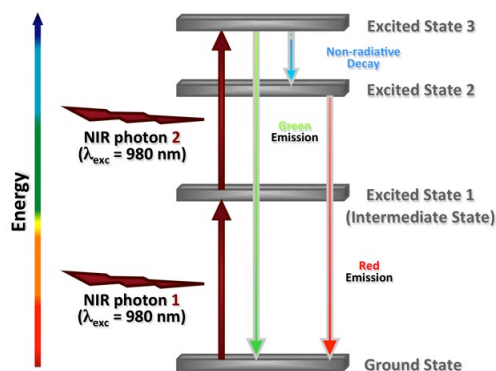


**Fig. 1:** Digital image of UCNPs doped with various lanthanide ions following 980 nm excitation.

nanomaterials are excited with near-infrared (NIR) light mitigating some of the drawbacks associated with the use of UV light as the excitation source. NIR light is silent to tissues thus minimizing autofluorescence, possesses greater tissue penetration capabilities and does not incur damage to the sample. Moreover, these nanomaterials require femtosecond (fs) excitation light to induce the multi-photon excited luminescence, which results in increased spatial resolution and hence, can be a valuable tool for deep tissue imaging. It is in this regard that there has been an ever-increasing interest in lanthanide ( $\text{Ln}^{3+}$ )-doped upconverting nanoparticles

(UCNP) as an alternative to more common multi-photon excited nanomaterials [1]. With UCNPs, it

is possible to obtain UV/visible/NIR emissions using a single NIR excitation source (typically 980 nm) via a process known as upconversion (Fig. 1). Upconversion is a multiphoton excitation process, however, unlike conventional two-photon excited materials where the absorption is simultaneous, the multitude of long-lived “real” electronic energy states of the  $\text{Ln}^{3+}$  ions (from the partially filled 4f shell) allow for sequential absorption of multiple NIR photons. Since these energy states possess long lifetimes, the need for complex and expensive optical excitation (fs laser) is eliminated and thus, upconversion can also be observed following excitation



**Fig. 2:** Schematic representation of the upconversion process in  $\text{Ln}^{3+}$ -doped materials.

with inexpensive low energy cw NIR diode lasers (Fig. 2). Here, we present the synthesis of upconverting  $\text{Ln}^{3+}$ -doped fluoride nanoparticles (such as  $\text{M}\text{LnF}_4$  where  $\text{M} = \text{Na}$  or  $\text{Li}$  and  $\text{Ln} = \text{Gd}$  or  $\text{Y}$ ), which are known to have the highest upconversion efficiency amongst UCNPs due to their low lattice vibrational energies (phonon energies). We show how these nanoparticles could be used as luminescent nanoprobes for the biological imaging of malignant cells. Moreover, through the inherent temperature dependence of their luminescence properties, we show they can be used as nanothermometers thereby paving the way towards a multi-modal nanoplatform.

## References

- [1] F. Vetrone, R. Naccache, A. Juarranz de la Fuente, F. Sanz-Rodríguez, A. Blázquez-Castro, E. Martín Rodríguez, D. Jaqué, J. García Solé, J. A. Capobianco, Intracellular Imaging of HeLa Cells by Non-Functionalized  $\text{NaYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$  Upconverting Nanoparticles, *Nanoscale*, **2**, 495-498 (2010)