

Finding a Single Lanthanide Ion through Upconversion

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Inorganic nanomaterials comprising lanthanide (also known as rare-earth element) dopant ions have been frequently used for applications in diverse fields ranging from biological labeling to solid-state quantum information storage.^[1] The application of these nanomaterials stems from electronic transitions within rich energy levels of the lanthanide ions, which arise from the tremendous complexity of the $4f^n$ configurations. For instance, the europium ion (Eu^{3+}) has been calculated to have more than 3000 energy levels.^[2] Subtle changes in the doping concentration, in the form of carefully planned and controlled experiments, can have a dramatic impact on the crystal structure, magnetism, and electronic and optical properties of the resulting materials.^[3] One example of this is the simultaneous tuning of the crystalline phase, morphology, and emission profile of NaYF_4 upconversion nanocrystals by introducing a variable quantity of lanthanide ions into the structure.^[4]

Despite the emerging prospects of lanthanide doping, the mapping and determination of the dopant concentration in nanocrystals or even bulk materials have been difficult to establish. Thus far, the reported concentration of a specific dopant ion in nanocrystals generally refers to the mole fraction calculated with the assumption that the lanthanide precursor is homogeneously dispersed in solution.^[5] The investigations are often hampered by the limited resolution of the instruments employed. Optical detection of a single nanoparticle doped with concentrated lanthanide ions can be realized relatively easily with a charge-coupled device camera, as the

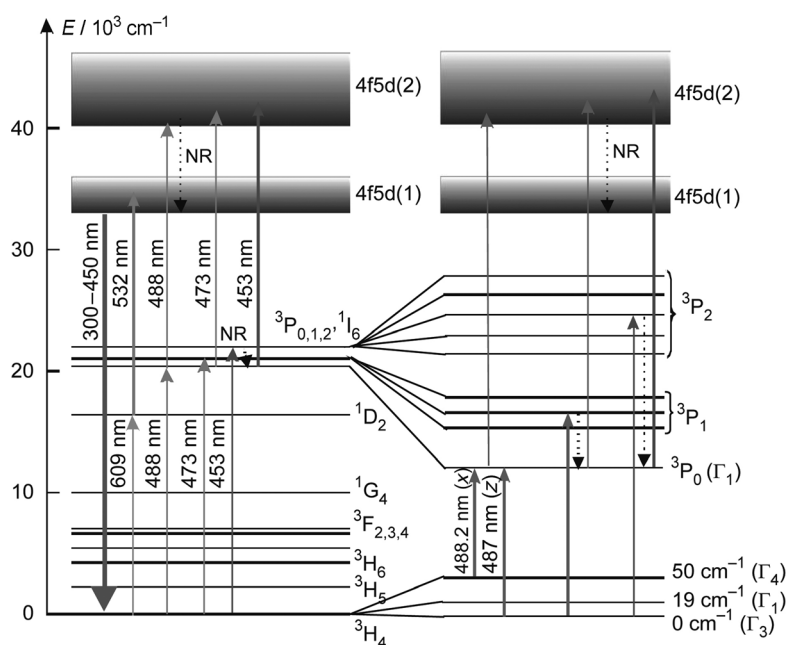


Figure 1. Proposed energy level diagram of the Pr^{3+} ion in a YAG crystal. Relevant optical transitions are indicated by arrows. NR refers to the non-radiative decay. Note that only the lowest three sublevels of $^3\text{H}_4$ manifold populated at room temperature are shown. Reproduced with permission from the Nature Publication Group.^[9]

dopant emitters collectively contribute to overall optical emission. In contrast, it is extremely challenging to directly observe the luminescence from a single or a few lanthanide ions because of the low luminescence brightness (the number of emitted photons per unit time).^[6] As a general rule of thumb, a short excited-state lifetime leads to a high brightness, while a long one suppresses the brightness. The spin-forbidden $4f^n$ – $4f^n$ electronic transitions of lanthanide ions give rise to long excited-state lifetimes in the range of milliseconds compared to nanoseconds for organic fluorophores and quantum dots.^[7] Another important factor limiting the luminescence brightness of single lanthanide ions is their low quantum efficiency.^[8]

Reporting in *Nature Communications*, Kolesov and co-workers demonstrated a powerful technique by which praseodymium can be detected at the level of individual ions in yttrium aluminium garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) nanocrystals.^[9] Their technique overcomes the intrinsic brightness problem of single Pr^{3+} emitters by promoting the $4f$ electrons onto the higher-lying $5d$ states, as the resulting parity-allowed $4f^n$ – $4f^n5d$ transitions have emission intensities up to 10 000 times stronger than the $4f^n$ – $4f^n$ transitions. In a YAG host material, the $(4f^2) ^1\text{S}_0$ level of Pr^{3+} lies above the lowest $4f5d$ band.^[10] As a result, only $4f5d$ band emission, in the ultraviolet spectral range of 300–450 nm, is observed (Figure 1). The high quantum efficien-

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cy (close to 100% even at room temperature) and very short lifetime (~ 19 ns) make this ultraviolet band emission particularly suitable for detecting single Pr^{3+} ions. Instead of directly pumping the electrons onto the 4f5d band with a deep-ultraviolet laser source (shorter than 300 nm), the authors exploited a two-step upconversion excitation process ($^3\text{P}_0$ as the intermediate state) under visible-laser illumination to realize a broadband ultraviolet emission (Figure 1). This visible-to-ultraviolet upconversion approach can lead to an increased signal strength by eliminating the background noise and thus provide better prospects for bioimaging use.^[11]

To determine the localization of single Pr^{3+} ions scarcely doped in YAG nanocrystals, the authors performed imaging studies using a high-resolution fluorescence microscope. Individual bright spots that correspond to Pr^{3+} optical centers appeared clearly on recorded fluorescent images. These bright spots were believed to be clusters of nanoparticles (Figure 2a). However, the photon-antibunching measurement (Figure 2b)—a superresolution technique arising from the tendency of fluorophores to emit photons in sequence rather than simultaneously—on several nanoparticles (marked in Figure 2a) suggested single-photon emission. The phenomenon of photon antibunching is a nonclassical optical property, routinely observed from a variety of single-quantum emitters, such as atoms, organic molecules, quantum dots, and nitrogen-vacancy centers.^[12] To verify the upconverted ultraviolet emission by a single Pr^{3+} ion, room-temperature excitation spectra of the upconversion emission were recorded. The spectra consisted of many sharp lines, indicating a high spectral selectivity of the upconversion process. Polarization dependence of the measured excitation spectra further proved the single-photon emitter behavior. Another notable demonstration by this research team was the rapid screening of Pr^{3+} ions site-specifically implanted in bulk YAG crystals.

Kolesov's and his colleagues' findings not only shed light on high-resolution bioimaging and quantum computing, but they also provide insights into the design of new treatment modalities for cancer. The authors showed that through the use of localized photochemical effects of lanthanide ions, site-specific

degradation of cancer cells can be achieved with high precision. However, in the real world, this photochemical process suffers from a low collection efficiency ($< 2\%$) of ultraviolet emission and is only applicable to the Pr^{3+} ion. Further work using different lanthanides, and a systematic investigation of Pr^{3+} doping in different host materials, must be undertaken to assess the potential technological impact of this exciting approach.

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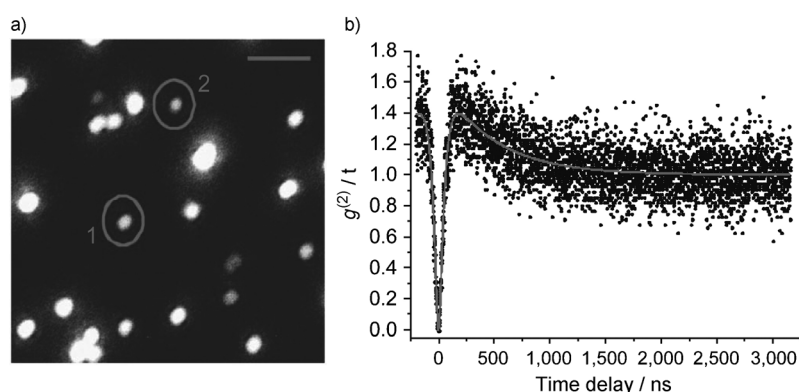


Figure 2. a) Fluorescence scanning ($10 \times 10 \mu\text{m}^2$ area) of YAG nanoparticles dispersed on a glass slide. Nanoparticles with single-photon emission are marked with circles. The scale bar is $2 \mu\text{m}$. b) The photon-antibunching measurement for the nanoparticle is marked with 1 in Figure 2a. Reproduced with permission from the Nature Publication Group.^[9]

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