

## **Luminescence Spectroscopy of Er<sup>3+</sup> Doped Inorganic Nanocrystals: An Investigation into their Upconversion Properties**

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It is very well known that the reduction of particle size of crystalline systems leads to important modifications of some of their bulk properties. Taking advantage of these size-induced changes, the design novel materials for advanced phosphor and photonic applications becomes possible. In particular, luminescent inorganic materials doped with trivalent lanthanide (Ln) ions have significantly enhanced optical properties when prepared at the nanoscale compared to the bulk. These include differences in luminescence efficiency, excited-state dynamics, and upconversion. My doctoral thesis presented a detailed investigation into the spectroscopic properties of novel luminescent inorganic nanocrystals doped with trivalent lanthanide (Ln) ions. When doped in inorganic materials, Ln ions can undergo a process known as upconversion, whereby they have the ability to (up)convert near-infrared (NIR) light to higher energy radiation such as visible or ultraviolet. This phenomenon has been known for quite some time in bulk glasses or crystals but until very recently, never observed in a nanomaterial. When you couple the small size of these materials (sub-20 nm) with the convenience of being able to emit visible light after absorbing low energy NIR light, a number of technological possibilities may be realized. Upconverting phosphors with nanosized dimensions have been extensively studied due to their applicability in light emitting devices, photonic based telecommunication, and biosensor development. The most viable is the development of a “sandwich-type” bioassay where the analyte of interest is wedged between donor and acceptor labels. This type of assay operates on the principle of fluorescence resonance energy transfer (FRET) where the donor label absorbs the excitation light and is followed by a radiationless transfer of energy to the acceptor where its emission is in turn detected. The size of the label is of critical importance since the distance over which FRET can operate is very limited and practically must be within a few nanometers for efficient energy transfer.

Conventional fluorescent sandwich assays, which use blue light to excite the donor label, have already been commercialized. However, the blue (high-energy) light absorbs readily by proteins (often damaging them) and also excites all fluorescent contaminants in the sample, resulting in poor sensitivity.

By replacing the donor label with an Ln-doped upconverting nanoparticle, it becomes feasible to use an NIR light source, which exclusively excites that label. However, before biomedical studies of such an assay could be performed, it is important to fully understand the mechanism that leads to upconversion in the nanosystems. As a result, we developed for the first time, erbium ( $\text{Er}^{3+}$ ) doped nanomaterials that are capable of upconverting NIR light to green and red. The  $\text{Er}^{3+}$  ion is ideal for use in FRET assays since it can emit upconverted green and red light after NIR excitation but more importantly, has no emission in the red region where the acceptor label would emit. Initially, we prepared simple  $\text{Er}^{3+}$ -doped binary nanocrystalline oxides ( $\text{M}_2\text{O}_3:\text{Er}^{3+}$  where  $\text{M} = \text{Y}, \text{Sc}, \text{or Lu}$ ) and studied the various parameters that may have an influence on the upconversion of the  $\text{Er}^{3+}$  ion: particle size, sample preparation, host structure, dopant ion concentration, etc.

We showed that after excitation with NIR radiation (980 nm) the nanocrystalline material emitted green and red light. However, when compared to an identically doped microcrystalline sample (bulk), the intensity of the nanocrystalline upconversion was several orders of magnitude lower. We discovered that this was due to the presence of contaminant species ( $\text{CO}_3^{2-}$  and  $\text{OH}^-$ ) bound to the surface of the nanoparticle that quenched the luminescence. We also proved that as a result of these species, the fundamental mechanisms of upconversion are significantly altered. Moreover, upconversion processes occur in the nanomaterial that do not exist in bulk systems. These differences were due to the large vibrational energies associated with  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  ( $3350$  and  $1500 \text{ cm}^{-1}$ ). In the bulk material, the largest vibrational energy available is that of the inorganic crystalline lattice ( $600 \text{ cm}^{-1}$ ). Thus, the larger vibrational energies available to the nanocrystalline lattice led to diverse radiative and non-radiative processes compared to the bulk. Consequently, drastically different upconversion spectra were obtained where for example, the nanocrystalline material has a stronger red emission than the bulk. This concentration dependent phenomenon was observed as the concentration of  $\text{Er}^{3+}$  was increased and as a result, we coined the term “enhancement of the red emission” to describe this since the intensity of the upconverted red emission increased by a greater factor than green light emission. Furthermore, changing the host material had a drastic effect. In nanocrystalline  $\text{Lu}_2\text{O}_3:\text{Er}^{3+}$ , the upconverted emissions were two orders of magnitude greater than identically doped  $\text{Y}_2\text{O}_3$  while  $\text{Sc}_2\text{O}_3$  showed a much more intense red

emission than either  $\text{Y}_2\text{O}_3$  or  $\text{Lu}_2\text{O}_3$ . These sesquioxides were the first nanomaterials to show upconversion.

After thoroughly understanding the mechanisms of upconversion in  $\text{Er}^{3+}$ -doped nanocrystals, the effect of codoping with ytterbium ( $\text{Yb}^{3+}$ ) was investigated. Upconversion in erbium/ytterbium codoped materials was well known in large systems but was not understood in nanomaterials. It was shown that adding  $\text{Yb}^{3+}$  to the system greatly enhanced the upconverted emission but the properties were quite diverse. We spectroscopically proved the presence of a mechanism in the nanocrystals, which does not exist in the bulk material and demonstrated that increasing the concentration of  $\text{Yb}^{3+}$  fundamentally changed the process by which upconversion occurred. In codoped nanomaterials or bulk materials with low  $\text{Yb}^{3+}$  concentrations, upconversion occurred via a two-step process but when the concentration of  $\text{Yb}^{3+}$  reached a saturation point in the nanocrystals, the mechanism changed to a three-step process.

We subsequently investigated the luminescent properties of more complex ternary nanocrystalline oxides (Gadolinium Gallium Garnet,  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ ) for the first time after a novel synthesis method was developed to prepare this well-known luminescent material in the nanoscale. When doped with  $\text{Er}^{3+}$ , we showed that the upconversion intensity of this material was unrivaled and several orders of magnitude greater than even the most intense binary oxide. The reason for the intense upconversion luminescence was determined to be due to the fact that GGG did not suffer from the inherent drawbacks of the binary oxides and thus possessed little or no surface contamination. As a result, their upconversion intensity was much stronger and is ideal for use in assays since upconversion emission was observed when pumping with low energy (5 mW) and inexpensive sources of NIR light (e.g. laser diode). After having grasped and fully elucidated the mechanisms of upconversion at the nanoscale, experiments are currently being carried out to coat the surface of the nanoparticle and bind it to a large biomolecule in order to study in more detail the energy transfer process between the nanoparticle and the biomolecule.