



Maximizing dopant photoluminescence in co-doped semiconductor nanoparticles for multiplex assays by tuning inter dopant electronic interactions: Synthetic co-doping or physical mixing of singly doped moieties?



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ABSTRACT

Evaluation of inter dopant electronic interactions is important to maximize photoluminescence for their use as multiplex assays. This work compares the photophysical properties of lanthanide dopants in cases where the lanthanide moieties have been either synthetically co-doped in nanoparticles or two singly doped nanoparticles were physically mixed post-synthetically. Nd^{3+} – Sm^{3+} and Nd^{3+} – Er^{3+} were considered as dopants in the TiO_2 nanoparticles. Remarkable differences in lanthanide emission have been observed between the two strategies of forming the multiple and distinct lanthanide containing assemblies. The inter lanthanide electronic interactions were found to be evident in the synthetic co-doping, with the same being absent in the physically mixed assembly. As a consequence, the Nd^{3+} emission in near infrared (NIR) and Sm^{3+} , Er^{3+} emission in visible spectral range respectively have been found to be more pronounced in the physically mixed assembly as compared to that in the synthetically co-doped nanoparticles. The situation is however reversed for the Er^{3+} emission in NIR spectral range. These findings collectively provide a facile way to maximize dopant emission and indicate the importance of tuning the inter lanthanide electronic interactions for better suitability as multiplex agent, in an as-desired way.

1. Introduction

The luminescence of trivalent lanthanide cations (Ln^{3+}) is emerging as an attractive alternative over conventional organic fluorophores due to the unique properties associated with the intra-configurational transitions of 4f electrons. These transitions produce sharp emission bands with negligible intra- and inter- Ln^{3+} spectral band overlap, spans entire visible and near infrared (NIR) spectral range, longer (microseconds – milliseconds) photoluminescence lifetime allowing time-gated data acquisition. In the perspective of data acquisition for longer time and improving signal-to-noise ratio, the resistance of Ln^{3+} emission to photo-bleaching mechanisms is of significant importance. The Ln^{3+} photoluminescence has been demonstrated for its usefulness in biological imaging, bio-analytical applications, sensing, optoelectronics, laser, and telecommunications; among others [1–3].

Despite various beneficial properties, the applications of Ln^{3+} photoluminescence for practical usefulness require significant effort in designing and optimizing the co-ordination environment. The extremely low ($<10 \text{ M}^{-1} \text{ cm}^{-1}$ as compared to $10^4 - 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for typical organic

fluorophores) molar extinction co-efficient of Ln^{3+} and quenching of Ln^{3+} emission by the vibrational overtones of –OH, –NH, –CH bonds pose restriction in this regard [1,4]. Two general approaches to develop novel Ln^{3+} containing luminophores include (i) designing an organic ligand based complex and (ii) incorporating Ln^{3+} in an appropriate assembly [5,6]. One of the major differences between these two approaches is in the number of Ln^{3+} , being generally few and multiple respectively. For example, in organic ligand based complexes one molecule has one to two lanthanide entities, with the multi-dentate nature fulfilled by multiple donor atoms in the ligand molecule [5,7–9]. On the other hand, a spherical titanium dioxide nanoparticle with 3 nm diameter and 5% nominal doping has fourteen dopant moieties [10,11]. In the linear range without contribution from concentration quenching, the incorporation of multiple Ln^{3+} in semiconductor nanoparticles along with the accessibility to low frequency lattice vibrations in inorganic structure is expected to maximize the Ln^{3+} emission. Besides this aspect associated with making the Ln^{3+} emission brighter, the incorporation of Ln^{3+} of different chemical identity and non-overlapping sharp emission bands has the potential to develop novel luminophore for multiplex assays.

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Lanthanide incorporated semiconductor nanoparticles is emerging as a novel class of host – guest materials, in which the nanoparticles with significant molar extinction co-efficient absorbs electromagnetic radiation and transfers energy to the Ln^{3+} center non-radiatively (an optical antenna effect), generating host (semiconductor nanoparticles) sensitized guest (Ln^{3+}) photoluminescence [12,13]. Towards the goal of developing lanthanide cation incorporated (doped) semiconductor nanoparticles, we have reported the photophysical properties of Ln^{3+} [$\text{Ln} = \text{Eu}, \text{Tb}$] incorporated hydrophobic II-VI sulfide and selenide [14], varying sized $\text{Zn}(\text{Tb})\text{S}$ [15], $\text{Zn}(\text{Tb})\text{S}$ with varying dopant extent [11], hydrophilic $\text{Zn}(\text{Ln})\text{S}$ [$\text{Ln} = \text{Sm}, \text{Eu}, \text{Tb}, \text{Dy}$] [16], $\text{Ti}(\text{Ln})\text{O}_2$ [$\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$] [17], near band gap matched $\text{Sn}(\text{Ln})\text{O}_2$ and $\text{Zn}(\text{Ln})\text{S}$ [$\text{Ln} = \text{Sm}, \text{Tb}$] [18] nanoparticles. Host sensitized Ln^{3+} emission was found to be most significant in the $\text{Zn}(\text{Tb})\text{S}$, $\text{Ti}(\text{Nd})\text{O}_2$ and $\text{Ti}(\text{Sm})\text{O}_2$ nanoparticles, the others comprise systems where the sensitized emission were either moderate or absent. The sensitization process have been rationalized considering the Ln^{3+} as charge (electron and/or hole) traps in the host material and the exciton recombination at these trap sites resulting in populating the Ln^{3+} luminescent energy level. Significant host sensitized dopant emission were realized in the cases where the Ln^{3+} ground and luminescent energy levels are optimally placed above and below the valence and conduction bands of the host material, so that the contribution from back charge transfer and auto-ionization is minimized [14,17,18]. Lanthanide emission in TiO_2 nanomaterials has also been reported previously [19,20].

Few researchers have reported the use of lanthanides for multiplex assays [21–23] and potentially revealing information from multiple locations to gain important insight in diagnostics. To this end, we have recently reported the photophysical characteristics in the synthetically co-doped $\text{Ti}(\text{NdSm})\text{O}_2$ and $\text{Ti}(\text{NdEr})\text{O}_2$ nanoparticles, and compared these to the ones in the corresponding singly Ln^{3+} incorporated counterparts, the $\text{Ti}(\text{Nd})\text{O}_2$ and $\text{Ti}(\text{Sm})\text{O}_2$ nanoparticles [24]. The Nd^{3+} and Sm^{3+} emission decreases by 6 and 4.5 times respectively in the co-doped nanoparticles, compared to that in the singly doped nanoparticles. The case with Er^{3+} reveals 3 times increase in 1550 nm emission efficiency in the synthetically co-doped case, with significant reduction in the visible emission centered at 565 and 665 nm respectively. The results have been rationalized within the framework of charge trapping mediated sensitization model and associated inter- Ln^{3+} electronic interaction governed by the spin selection rule. Although the $\text{Ti}(\text{NdSm})\text{O}_2$ nanoparticles provide an avenue for generation of six distinct emission spanning orange – red and NIR spectral range simultaneously, an improvement of the Ln^{3+} emission efficiency would provide better applicability of the multiple and distinct lanthanide containing systems as multiplexing agent.

Examining the possibility for improvement of the lanthanide emission efficiency as the primary objective, this work compares the photoluminescence characteristics of the $\text{Ti}(\text{NdSm})\text{O}_2$ nanoparticles that has been reported in our earlier work [24] and a physical mixing of the $\text{Ti}(\text{Nd})\text{O}_2$ and $\text{Ti}(\text{Sm})\text{O}_2$ nanoparticles to generate the $\text{Ti}(\text{Nd})\text{O}_2 - \text{Ti}(\text{Sm})\text{O}_2$ composite system. The generality of the observations have been tested and verified with the corresponding nanoparticles containing Nd^{3+} and Er^{3+} as the two lanthanide moieties. Mahalingam and co-workers [25] have demonstrated inter-particle energy transfer in sub-5 nm Ln^{3+} doped BaLuF_5 nanocrystals [25]. Lin and co-workers [26] reported how photophysical properties of a material can change when the components have been treated differently to make the composite assembly. These studies indicate that it is indeed possible to access unique photophysical properties when the components are mixed post-synthetically. The motivation of the current strategy of mixing two nanoparticles post-synthetically relies on examining the possibility of tuning the inter Ln^{3+} electronic interactions when the two Ln^{3+} are either present in one nanoparticle (synthetic co-doping) or present in two different nanoparticles (physical mixing).

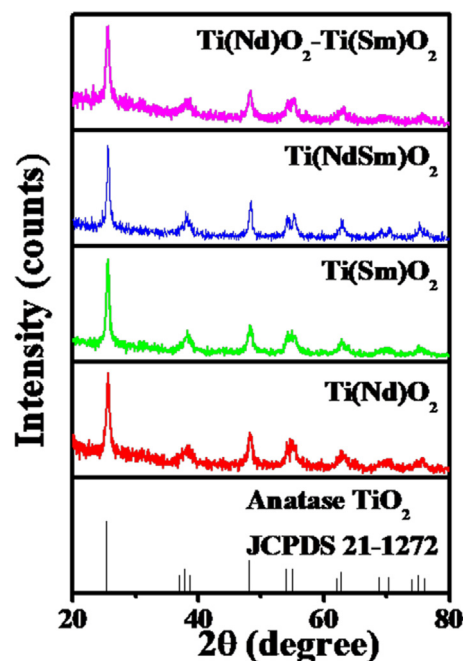


Fig. 1. XRD profiles for the nanoparticles studied are shown. The profiles for the $\text{Ti}(\text{Nd})\text{O}_2$, $\text{Ti}(\text{Sm})\text{O}_2$ and $\text{Ti}(\text{NdSm})\text{O}_2$ nanoparticles have been first reported in our previous study [24].

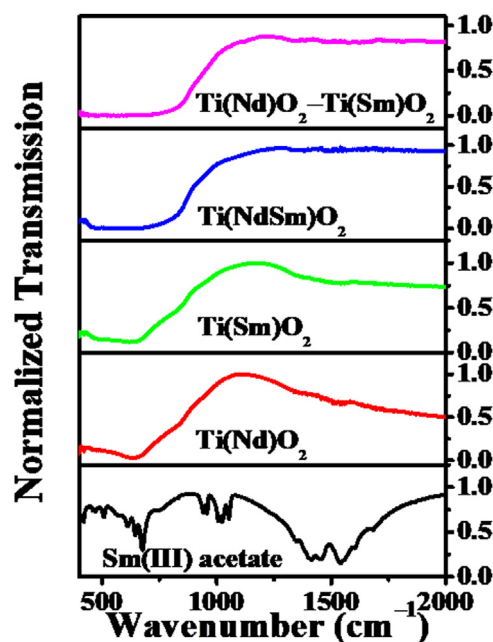


Fig. 2. FTIR spectra of different systems studied are shown.

2. Materials and methods

2.1. Chemicals

Tetra(*n*-butyl) titanate and lanthanide acetate hydrates ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Er}$) (99.9%) were purchased from Alfa Aesar. Ethanol was purchased from Merck. Potassium bromide (KBr) IR grade and coumarin 153 (C153) were purchased from Sigma-Aldrich. All chemicals were used as purchased without performing any additional purification. Water used for all experiments was obtained from a Millipore system with resistivity of 18.2 $\text{M}\Omega \text{ cm}$ at 25 °C.

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