Particle size dependence of the dynamic photophysical properties of NaYF₄:Yb, Er nanocrystals

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Abstract: The effects of the nanocrystal size on the emission spectra and decay rates of upconverting hexagonal NaYF₄:Yb,Er nanocrystals are investigated. The influence of nanocrystal size is represented in terms of the surface area/volume ratio (SA/Vol). Our results show that a small nanocrystal size, or large SA/Vol ratio increases the decay rate, in particular, the green luminescence decay rate varies linearly with the SA/Vol ratio.

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1. Introduction

The use of upconverting rare earths in a solid state infrared quantum counter was first proposed by Blömberger [1] and subsequently demonstrated by Auzel et al. using a doubly doped tungstate host [2]. Later, Brown et al. used singly doped SrF₂ [3] to confirm that successive photons were absorbed, resulting in emission at a higher energy. The role played by energy transfer upconversion (ETU) was verified by Auzel et al., who found that the Yb³⁺ ion transfers energy to the Er³⁺ ion [4]. Upconversion emission from Tb³⁺, Ho³⁺, Er³⁺ and Tm³⁺ ions, sensitized by Yb³⁺, have been observed in silicates [5] and oxides, such as zirconium oxide [6], silica [7], yttrium oxide [8, 9], as well as oxysulfide [10].

Much research in upconversion luminescence has also been conducted in II-VI semiconductor quantum dots such as CdS [11, 12], CdTe [13, 14], CdSe [15] among others. These materials have also been shown to upconvert by a multi-photon mechanism. However, there are fundamental differences between the semiconductor upconverters and the lanthanide doped upconverters emphasized in this study. One is that upconversion in the former operates via a virtual, or weakly allowed intermediate state. Hence, upconversion luminescence lifetimes are in the order of tens of nanoseconds compared to hundreds of microseconds in lanthanide doped upconverters which operate via real, long-lived intermediate states. In practical terms, this mean that semiconductor upconverters are more efficiently excited by nanosecond pulsed laser sources while lanthanide doped upconverters are efficiently excited by CW sources (the laser pulses in this publication were on order of 100 microseconds).

In addition, while the absorption of the semiconductor upconverters are tunable by nanocrystal size, the absorption of the fluoride nanocrystals are dependent on the sensitizer absorption (Yb³⁺), which absorbs at a fixed wavelength. Lastly, the chemical structure of the lanthanide based upconverters emit from the 4f shells of the rare earths, which are efficiently shielded from their chemical environment by the outerlying 5s and 5p electrons. As a result, the emission lines are quite sharp, 10 nm or less in width compared to the broader emission from semiconductor based upconverters.

Some researchers have shown applications as reporters [10, 16–19], biolabels [20–22], emissive displays [23], solar cells [24], and even microbarcodes [25]. Recently, the emergence of low phonon energy hosts such as chlorides, bromides and fluorides [26–31] have increased the competitiveness of upconverting nanocrystals (UCNPs), making them much brighter at smaller sizes. NaYF₄:Yb, Er is known as one of the brightest upconverting phosphors [32, 33]. It has been shown that they can be synthesized in solution at sizes down to 10 nm [34–38], especially in the more efficient hexagonal NaYF₄ form [19, 22, 38, 39]. The reduction of particle size in a crystalline system can result in modifications of their bulk properties because of the high surface area-to-volume (SA/Vol) ratio. However, the
dependence of photo-physical properties on NaYF₄ nanocrystal size, especially approaching 10 nm or smaller has not been well understood. Various researchers have reported not only a size dependence, but also a shape dependence on luminescent properties [40, 41]. We have attempted to address the size and to a lesser extent shape dependence on upconversion luminescence and dynamics. Our results indicate that the luminescent decay rate is highly dependent on the mean distance of excited ions to the surface of the nanocrystal. This is attributed to the nanocrystal surface acting as boundaries to energy transfer to intermediate states. The increase in green emission has been attributed to phonon confinement in smaller nanocrystal sizes, thereby affecting non-radiative phonon relaxation.

2. Experiment

Hexagonal UCNPs were synthesized according to the procedure outlined in the work of Shan et al. [38]. In our study, hexagonal structured UCNPs of two different shapes were used: Two samples are of spherical shape, which are samples #1 and #4 respectively, as shown in Fig. 1(a) and (d), and two are of rod shape, which are samples #2 and #3 respectively, as shown in Fig. 1(b) and (c). The SA/Vol ratio and dimensions are illustrated in Table 1.

![Fig. 1. (a) to (d), TEM images of sample a) #1, spherical-shape, SA/Vol = 0.14 nm⁻¹, b) #2, rod-shape, SA/Vol = 0.10 nm⁻¹, aspect ratio = 3.3, c) #3, rod-shape, SA/Vol = 0.04 nm⁻¹, aspect ratio = 1.7, and d) #4, spherical, SA/Vol = 0.02 nm⁻¹.](image)

Table 1. The physical properties and emission characteristics of samples #1 to #4.

| Sample | #1   | #2   | #3   | #4   |
|--------|------|------|------|------|
| SA/Vol | 0.14 | 0.10 | 0.04 | 0.02 |
| Shape  | Spherical | Rod | Rod | Spherical |
| Dimensions | 10 nm | 63 nm by 19 nm | 89 nm by 54 nm | 130 nm |
| Aspect ratio | - | 3.3 | 1.7 | - |
| Yb/Er ratio | 18.5 | 10.8 | 11.7 | 10.7 |
| Green/Red | 1.2 | 3.9 | 2.0 | 1.7 |

Sample holders were constructed by sandwiching a one-inch square coverslip, which has a 5 mm by 5 mm square shaped opening machined by sand blasting methods, in between two other coverslips. The UCNPs are usually packed into the opening before sealing with the third
coverslip. By using this configuration, the sample area was kept at 5 mm by 5 mm square and a constant sample depth of 170 microns, which is also the thickness of the sandwiched coverslip.

The samples were excited using a collimated 975 nm diode laser (Qphotonics), which was driven with a laser diode driver (Thorlabs LDC3065-488). The IR intensities were varied using neutral density filters. The emission spectra were collected by an XY translation mounted fiber coupled to a spectrometer (Ocean Optics USB2000). The time-resolved measurements were conducted with the same diode laser, driven by a pulsed laser diode driver (EO Devices ETX-10A-C), which was triggered by a pulse generator. The luminescence was dispersed by a monochromator before detection by a photomultiplier tube (Hamamatsu R928). The decay curves were collected by a digital oscilloscope (Tektronix TDS3052B) with averaging.

3. Results and discussion

The emission spectra of samples #1 to #4 are shown in Fig. 2(a) and (b) and their corresponding energy transitions demonstrated in Fig. 2(d) [42]. The green emission in Fig. 2(a) consist of an emission band from 520 nm to 535 nm is attributed to transition from the Er$^{3+}$: $^2$H$_{11/2}$ level to the Er$^{3+}$: $^4$I$_{15/2}$ ground state, and an emission band from 540 nm to 560 nm is assigned to the Er$^{3+}$: $^4$S$_{3/2}$ level transition to the ground state. The red emission in Fig. 2(b) from 635 to 685 nm is attributed to the Er$^{3+}$: $^4$F$_{9/2}$ level decaying to the ground level. The luminescence of sample #4 is much higher than the rest, and hence the intensity has been rescaled in order to permit plotting of all four curves together.

We have observed a difference in the relative green/red emission over all four samples. In Fig. 2(c), the amounts of green over red emission (G/R ratio), calculated by integrating the area under the peaks for green and red emission separately, are plotted against the SA/Vol (nm$^{-1}$) ratio. The G/R ratio appears to increase with the SA/Vol ratio in samples #4 to 2 and then decreases drastically in sample #1. This dramatic decrease may be attributed to the larger Yb/Er ratio in this sample, while the Yb/Er ratio is nearly constant among the other samples. Our observation is in contrast to the more commonly observed increase in red emission with decreasing nanoparticle size, which is attributed to surface defects in the case of codoped yttrium oxide based upconverting nanocrystals [41, 43–46]. Our observation of greater green emission with reduction in nanocrystal size, agrees with the report of Shietinger et al. [47] (Fig. 4b in their paper). It thus appears that there is a determinant inherent to the nanocrystal source, which is yet to be identified, although we note that the majority of “greater red/green emission” reports use oxide materials, while our nanocrystals were based on fluorides (as in Shietinger’s case). Shietinger et al. have also hypothesized that size confinement of phonon modes, that is the reduction of phonon modes with size, affect upconversion spectra by reducing non-radiative phonon relaxation (see also Chen et al. [48]), leading overall to a higher relative population of the green emissive state.

To test this hypothesis, we have performed low-temperature time resolved studies (not shown) on a rod-shaped sample of comparable size and found upon cooling to 77K, that ‘hot’ lines are absent and there is neither any discernable change in the decay characteristics nor spectra as seen by other researchers [49]. Hence, we do not have convincing evidence of phonon coupling for example to surface hydroxyl groups, in our rod-shaped samples. We also note that in sample #1, Yb/Er ratio is slightly higher than in the rest, which would then account for the more red emission, in line with observations with other researchers [50–52].

We also want to bring to attention the shape and size studies conducted by Zhang et al. [53], with nanorod, nanotube and nanodisk UCNPs. We note that the structures produced were novel, especially with regards to nanotubes linked in a honeycomb lattice and the windmill type patterns on their nanodisks. The complexity of their nanocrystals does not easily accommodate a straightforward comparison with our UCNPs.
Fig. 2. Emission spectra of sample #1 to #4 under 980 nm excitation, where a) shows emission between 500 and 575 nm, b) shows emission between 630 and 700 nm, c) shows a plot of Green/Red (GR) ratio and Yb/Er dopant ratio as a function of the SA/Vol, and d) schematic diagram of Yb$^{3+}$ sensitized Er$^{3+}$ upconversion luminescence under 980 nm excitation.

The relative intensity of the two green bands can be understood by considering the energy separation between the nearest excited states Er: $^2\text{H}_{11/2}$ and Er: $^4\text{S}_{3/2}$, which is only several hundred wavenumbers. Thus, the population distribution on Er: $^2\text{H}_{11/2}$ and Er: $^4\text{S}_{3/2}$ should be dominated both by thermal distribution and nonradiative relaxation. Therefore, the population of the Er: $^2\text{H}_{11/2}$ level varies as a function of the Boltzmann’s distribution [51]. Since an increase in Yb$^{3+}$ concentration gives rise to higher IR absorption and generation of thermal energy, increased thermal energy should enhance population of the Er: $^2\text{H}_{11/2}$ level [40]. This is corroborated by our observations in sample #1, where Yb/Er ratio is the largest, the ratio of Er: $^2\text{H}_{11/2}$ over $^4\text{S}_{3/2}$ is also the highest at 0.29, whereas for samples #2-4, where doping concentrations are similar, the same ratios are more similar. In our cooling experiments (not shown), we do observe decrease of the transition from Er: $^2\text{H}_{11/2}$ with cooling to 75K.

Figure 3(a) shows the time-resolved emission at 550 nm of all the samples. In general, the sample luminescence decay show increasing rise times with increase in size. We performed fitting of the decay curves with a series of self-consistent rate equations and an example of a fit is shown for sample #4 in Fig. 3(b). The fitted decay rates are plotted against the SA/Vol (nm$^{-1}$) ratio as shown in Fig. 3(c).
It is clearly observable that the green luminescence decay rate is linear to the SA/Vol ratio. The decay rate is thus highly dependent on the mean distance of excited ions to the surface of the nanocrystal. This could be due to the hindrance of resonant energy transfer from short-lived to long-lived intermediates by nanocrystal boundaries, or the presence of traps at the nanocrystal surface and also by the reduction of the phonon modes and consequently phonon-mediated energy transfer [48]. These models not only explain why the smallest nanocrystals decay the fastest, but also why they tend to give dimmer emission. From the linear increase we can infer that the mean free transfer distance in bulk materials is larger than the largest Vol/SA ratio in this study. This is due to crystal boundary and phonon confinement restrictions in the nanocrystals. We obtain strong evidence that the critical transfer is from Yb to Er ions from Fig. 3(d), since the Yb/Er dopant ratio is more closely correlated to the energy transfer rate than the SA/Vol ratio.

Further clues about the energy transfer with the sample can be gained from the log-log curves of emission intensity versus pump power, which are plotted in Figs. 4(a) for green and (b) red emission. We note that on average, the slope of the red emission (slope = 2.4) is slightly larger than that of the green emission (slope = 2.0). That is because the Er: 4F_{9/2} level can be populated both by multiphonon relaxation from the Er: 4S_{3/2} levels, as well as energy transfer from a neighboring ion, which accounts for a slope of mixed two- and three-photon character [54].
The slopes of the curves in Figs. 4 (a) and (b) are presented as a function of the SA/Vol ratio in Figs. 4 (c) and (d). The onset of saturation is observed at much lower pump intensities in the nanocrystals which have a lower SA/Vol ratio, and which are also larger. At pump powers below 100 mW, there is little correlation between the slope and the SA/Vol. Only at 1W do we see a significant change in slope with SA/Vol, with the slope increasing as the SA/Vol decreases, an effect also observed by other researchers [43, 55].

Our observation of upconversion saturation is consistent with the depletion of the Er: $^4I_{11/2}$ level [56]. We can attribute the SA/Vol dependence to the same two mechanisms we discussed in the previous section. In particular, a disruption of the Yb to Er transfer by grain boundaries in high SA/Vol samples leads to a lower upconversion rate of occupied Er: $^4I_{11/2}$ levels. Similarly, a rapid depopulation of any of the excited states involved in the upconversion pathway due to surface states of high SA/Vol samples would also reduce the upconversion rate. In both cases, the reduced upconversion rate would prevent the depletion of Er ions in the $^4I_{11/2}$ state, and thus these samples do not display saturation in our experiments.

4. Conclusion

In the light of these observations, the nanocrystal size clearly affects luminescence lifetime, intensity and emission color. While it has been observed by other researchers that red emission increases with decrease in nanocrystal size [43, 57], attributed to hydroxyl and carboxyl defects on the surface [41], in general, we have seen the opposite, of increasing green emission with decreasing size. Specifically, we have found that the green luminescence decay rate is linearly dependent on the nanocrystal size and postulated that the nanocrystal surfaces act as boundaries to energy transfer to intermediate states. The increase in green emission has been attributed to phonon confinement in smaller nanocrystal sizes, thereby affecting non-radiative phonon relaxation.

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