Structure design and applications of upconversion nanoparticles

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Chapter 3
Employing Shell to Eliminate Concentration Quenching in Photonic Upconversion Nanostructure*

It is generally accepted that for lanthanide ions based upconversion material low doping is necessary to reach a relatively high upconversion emission (normally < 3 mol%), because of the concentration quenching effect. Here, we demonstrate that this limitation can be broken in nanostructures. Simply by an inert shell coating strategy, the concentration quenching effect for activator (Er³⁺) could be eliminated and highly efficient upconversion luminescence is realized in the activator fully doped (also named “dopant free”) nanostructure, e.g. NaErF₄@NaYF₄. More importantly, this novel nanostructure achieves some long-cherished desires, such as multiple-band co-excitation (~ 800 nm, ~ 980 nm and ~ 1530 nm) and monochromic red emission. Proof of concept experiments are presented for the potential benefit of this structure in solar cell and anti-counterfeiting. This nanostructure also offers new possibilities in realizing high upconversion emission and novel functionalities of lanthanide based nanomaterials.

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3.1 Introduction

Since the mid-1960s, lanthanide ions (Ln\(^{3+}\)) doped materials have displayed attractive potentiality in numerous fields (solar cell, biology, display and security etc.),\(^{1-12}\) due to its unique luminescent property of converting near-infrared (NIR) photons to ultraviolet (UV) or visible (VIS) photons. For this material, one of the most important issues is to identify the optimal host-dopant combinations to obtain the high efficient upconversion (UC) emission. To date, almost all the efficient UC systems adopt the sensitizer/activator co-doping strategy, and usually the doping concentration of activator remains at a low level (e.g. below 3 mol%).\(^{13-14}\) This status is mainly attributed to the following inherent points of view. Over the years, it is generally believed that it is difficult to observe efficient UC emission without the help of sensitizer ions (e.g. Yb\(^{3+}\), Nd\(^{3+}\)), due to the limitation of the insufficient absorption ability of activator. In the meantime, the compensation method for this issue, i.e. raising the concentration of activator, is considered likely to trigger the negative concentration quenching effect (the high doping concentration will lead to harmful cascade energy migration and cross-relaxation between dopant ions, thus increases the probability for excited state energy to be trapped by the quenching sites).\(^{15}\) Until now, only limited improvements have been made in suppressing the concentration quenching effect, such as the spatially doping strategy,\(^{16-18}\) forming ions cluster in nanostructure\(^{19}\) and utilizing ultra-high excitation irradiiance (~10\(^6\) W/cm\(^2\)).\(^{20-21}\) However, the fundamental issues to further improve the optimal concentration of activator remain far from resolved. The relevant mechanism is still puzzled. In practice, under the traditional low excitation power density (<10\(^3\) W/cm\(^2\)), the UC efficiency for activator heavily-doped nanosystems is still at least one order of magnitude lower than the widely accepted activator low-doping systems (e.g. NaYF\(_4\): 20% Yb, 2% Er@NaYF\(_4\), upon the excitation of 980 nm).\(^{22-23}\)

Herein, we report an efficient core-inert shell UC nanostructure, which strongly suppresses the concentration quenching effect of activator (Er\(^{3+}\)) in the luminescent core area, enables the optimal doping concentration of Er\(^{3+}\) in the core up to 100 mol%. Interestingly, this activator “fully-doped” core-inert shell nanostructure i.e. NaErF\(_4\)@NaYF\(_4\) and its relevant derivatives (e.g. NaErF\(_4\): 0.5% Tm@NaYF\(_4\)) exhibited many unique UC properties, such as high luminescent efficiency (typically, the efficiency is about 0.1-1% under 100 W/cm\(^2\) 980 nm laser excitation, and about 1-5% under 10 W/cm\(^2\) 1530 nm laser excitation), multi-band excitation in the NIR region (~ 800 nm, ~ 980 nm, ~ 1530 nm) and monochromic red emission (~ 650 nm). Steady-state and time-resolved spectroscopic studies unravel that the suppression of concentration quenching effect comes from the minimized quenching sites and increase of the activator. Furthermore, the advantages of this multi-band excitable UC structure in the potential applications like solar cell and anti-counterfeiting have been demonstrated by proof of concept experiments.

3.2 Results and discussion

3.2.1 Basic characterization of nanostructures

The core-shell nanoparticles were synthesized through a typical procedure.\(^{25}\) Taking NaErF\(_4\)@NaYF\(_4\) as an example, the uniformed size and morphology of nanoparticles before and
after shell coating was revealed by the low-resolution transmission electron microscopy (TEM) imaging (Figure 3.1a, b). The diameters of core and core-shell nanoparticle were confirmed to 20 ± 1 nm and 30 ± 2 nm, respectively, as shown in the high-resolution TEM imaging (Figure 3.1a, b insets). The shell thickness (5 nm) was verified by the high angle annular dark field (HAADF) image (Figure 3.1c). HAADF is a STEM technique where the brightness of the imaging point is proportional to the square of the atomic number of the on-site element. The heavier lanthanide elements (Er, brighter parts) and the lighter ones (Y, darker parts) of the nanoparticle can thus be distinguished. In addition, the crystal structures of NaErF$_4$ bare core and NaErF$_4$@NaYF$_4$ core-shell were confirmed as pure hexagonal-phase structure by X-ray powder diffraction (XRD) results, as shown in Figure 3.1d (contrast with the standard hexagonal structure of NaYF$_4$ nanoparticles, Joint Committee on Powder Diffraction Standards file number 16-0334).

**Figure 3.1** Structure characterization of NaErF$_4$ and NaErF$_4$@NaYF$_4$ nanoparticles. The low-resolution TEM and high-resolution TEM (inset) images of (a) the NaErF$_4$ bare core nanoparticles, (b) the as-prepared NaErF$_4$@NaYF$_4$ core-shell nanoparticles. (c) Typical high angle annular dark field (HAADF) image of the NaErF$_4$@NaYF$_4$ core-shell nanoparticle. (d) Corresponding powder XRD diffraction patterns of the NaErF$_4$ and NaErF$_4$@NaYF$_4$ nanoparticles, contrast with the standard hexagonal structure of NaYF$_4$ nanoparticles.

Furthermore, the Er$^{3+}$ dopant concentrations of core and core-shell nanostructures were confirmed by the energy dispersive spectrometer (EDS) results which measures the characteristic emission of elements under the X-ray radiation. As shown in the Figure 3.2, in the NaErF$_4$ bare core, the atom ratio of Er:Y is over 90:1, while in the NaErF$_4$@NaYF$_4$ core-shell nanoparticle,
the atom ratio of Er:Y is 0.38:1. These results are consistent with the calculation results relies on the uniformed core (20 nm) size and shell thickness (5 nm).

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**Figure 3.2** The element analysis results of (a) NaErF₄ bare core and (b) NaErF₄@NaYF₄ core-shell nanoparticle.

### 3.2.2 Spectroscopic properties of NaErF₄@NaYF₄ nanostructure

Different from the traditional sensitizer-activator co-doping systems, which usually are effectively only on one specific excitation wavelength (e.g. ~ 800 nm, ~ 980 nm or ~ 1530 nm), because of the unique ladder-like energy levels of Er³⁺, the NaErF₄@NaYF₄ core-shell nanostructure has the ability to obtain efficient UC emission under all of these three excitation wavelengths in NIR region. To evaluate its UC properties, comparisons have been conducted between NaErF₄@NaYF₄ nanoparticles and three recognized efficient nanostructures under different excitation wavelengths (i.e. NaYF₄: 20% Yb, 2% Er@NaYF₄: 20%Yb@NaYF₄: 10% Nd nanoparticle under the excitation of 800 nm, NaYF₄: 20% Yb, 2% Er@NaYF₄ nanoparticle under the excitation of 980 nm and NaYF₄: 20% Er@NaYF₄ nanoparticle under the excitation of 1530 nm, all the contrast samples have the similar structure with ~ 20 nm core and ~ 5 nm shell). As shown in the Figure 3.3 a-c, the UC emission (especially the red emission band) of NaErF₄@NaYF₄ nanoparticle is as strong as those under 800 nm or 980 nm excitation (10 W/cm²) or even exceeds with an order of magnitude (under 1 W/cm² 1530 nm excitation) of its counterparts. It is also worth noticing that, within the visible spectral range, the UC emission of the NaErF₄@NaYF₄ nanostructure always owns a relatively high red/green (R/G) ratio (over 10 times, Figure 3.3d).
Figure 3.3 UC emission spectra of cyclohexane solutions containing NaErF₄@NaYF₄ nanoparticles with the corresponding contrasts (a) 800 nm excitation (10 W/cm²), (b) 980 nm excitation (10 W/cm²) (c) 1530 nm excitation (1 W/cm²). Insets a-c: the luminescent photos of cyclohexane solutions containing NaErF₄@NaYF₄ (monochromic red emission) and its counterparts, respectively. (d) The R/G ratios of NaErF₄@NaYF₄ nanoparticle under the 800 nm, 980 nm and 1530 nm excitation, respectively.

This character can be attributed to the efficient cross relaxation (CR) interactions between Er³⁺ ions in vicinity, i.e. CR₈₀₀ₑₓ: 2⁴I₉/₂ → ⁴S₃/₂ + ⁴I₁₃/₂ and ⁴S₃/₂ + ⁴I₉/₂ → 2 ⁴F₈/₂, CR₉₈₀ₑₓ: ⁴F₇/₂ + ⁴I₁₁/₂ → 2 ⁴F₉/₂ and CR₁₅₃₀ₑₓ: ⁴S₃/₂ + ⁴I₉/₂ → 2 ⁴F₉/₂. Furthermore, utilizing the energy transfer between Er³⁺-Tm³⁺, it is determined that through a feasible improvement strategy to drive down the green emission, the R/G ratio could be further enhanced to over 50, thus achieving the efficient monochromic red emission. As shown in the Figure 3.4 a-c, doping 0.5% Tm into the core area results in a significant enhancement of all the R/G (red/green) ratios, e.g. from 38.5 to 80.2 under 800 nm excitation, from 20.1 to 86.1 under 980 nm excitation and from 11.8 to 50 under 1530 nm excitation, respectively. In the meantime the overall UC emission intensity does not show obvious change. This phenomenon can be attributed to the energy transfer between Er³⁺ and Tm³⁺ as indicated in Figure 3.4d, which reduces the green emission of Er³⁺ effectively.
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Figure 3.4 The UC emission spectra of NaErF₄@NaYF₄ and NaErF₄: 0.5% Tm@NaYF₄ nanoparticles under the excitation of (a) 800 nm (10 W/cm²), (b) 980 nm (10 W/cm²) and (c) 1530 nm (1 W/cm²), respectively. (d) The schematic of the energy transfer process between Er³⁺ and Tm³⁺.

The unique properties of the NaErF₄@NaYF₄ nanostructure may be understood as follows. Firstly, the absorption of the nanoparticle gets up to be comparable with the traditional sensitizer (Yb³⁺ or Nd³⁺) co-doped nanoparticle due to the Er³⁺ concentration being lifted up to 100 mol%. As shown in the Figure 3.5, the absorption of NaErF₄@NaYF₄ nanoparticle reaches 33% of the NaYF₄: 10% Nd nanoparticle (integration from 770 nm to 830 nm) and 120% of the NaYF₄: 20% Yb nanoparticle (integration from 920 nm to 1040 nm). The absorption data were collected by a standard UV-Visible spectrometer.
Figure 3.5 The absorption spectra of NaErF₄@NaYF₄ core-shell nanoparticles, NaYF₄: 10% Nd bare core and NaYF₄: 20% Yb bare core nanoparticles (normalized by the concentration of the nanoparticles in cyclohexane).

Secondly, the strong UC emission of NaErF₄@NaYF₄ nanoparticles suggests that the concentration quenching effect is effectively suppressed. From the traditional understanding, the doping concentration increasing shall inevitably promote the cascade energy migration and cross relaxation process between activators and/or sensitizers and the excited state energy has thus more probability to be captured by the quenching sites in the particle, resulting in the quench of the UC emission.\textsuperscript{15, 34} However, what about it if the quenching sites are very few or an ideal case, \textit{i.e.} “quenching site free”? In these cases the high mobility of excited states as induced by the high concentration of activator is actually not so harmful, or even benefit to the UC efficiency by promoting the interaction of the excited states (Figure 3.6a).
To simply the discussion, we assume here that the NaErF$_4$@NaYF$_4$ core-shell nanostructure is a “quenching site free” system. This assumption is reasonable since the core is only made up of a few crystal lattices compared with bulk material, thus it is possible to form a luminescent core area without quenching site inside. In addition, by blocking the energy dissipation path from luminescent core to the surface with the shell NaYF$_4$, the surface quenching sites of nanoparticle could be deactivated. To validate this argument, we intentionally introduced quenching sites into the nanoparticle. As shown in Figure 3.7 and 3.8, either the NaErF$_4$ bare core which contains numerous quenching sites on the particle surface or NaErF$_4$: 0.5% Nd$^{3+}$@NaYF$_4$ core-shell nanoparticle where Nd$^{3+}$ plays the role of bulk quenching sites, deteriorated concentration quenching effect occurred.
Figure 3.7 The shell thickness dependent UC emission intensity (integration from 500 nm to 700 nm) of NaErF₄@NaYF₄ nanostructure (0 nm shell corresponding to the NaErF₄ bare core), the excitation wavelength is (a) 800 nm (10 W/cm²), (b) 980 nm (10 W/cm²) and (c) 1530 nm (1 W/cm²), respectively.

Figure 3.8 The UC emission spectra of the NaErF₄@NaYF₄ (20 nm core and 5 nm shell) and NaErF₄: 0.5 mol% Nd@NaYF₄ (20 nm core and 5 nm shell) nanoparticle under (a) 800 nm, (b) 980 nm and (c) 1530 nm excitation, respectively.

To further demonstrate that the concentration quenching effect could be controlled by the environment of activators (e.g. surface quenching sites), a series of comparisons between singly doped bare core (NaYF₄: x% Er³⁺, x: 2-100) and core-inert shell (NaYF₄: x% Er³⁺@NaYF₄, x: 2-100) nanoparticles have been conducted (Figure 3.9). 980 nm excitation was taken as an example (similar results obtained under 800 nm and 1530 nm excitation are shown in Figure 3.10 and Figure 3.11). For the bare core structure, the optimal doping concentration of Er³⁺ is limited to 2-20 mol% (Figure 3.9a), which is in line with previous reports, and the Er³⁺ heavily doped nanoparticles exhibit very weak UC emission, especially for the NaErF₄ bare core almost no UC emission was detected. However, the NaYF₄ shell coating promotes the optimal concentration to 100 mol% (Figure 3.9b), where the brightest UC emission could be observed from the NaErF₄@NaYF₄ nanoparticles. These results indicate that in the bare core structure, the concentration quenching phenomenon is mainly induced by the energy dissipation from activators to the surface quenching sites. Be more specific, doping concentration increase decreases the distance between Er³⁺ ions and leads to more efficient energy migration and cross relaxation.
process between Er\(^{3+}\). In the presence of numerous surface quenching sites, \textit{i.e.} for bare core, this will enhance the possibility of excited state energy being trapped by surface quenching sites, so dim the UC emission.\(^{36-37}\) Situation is different for core-inert shell structure, where the coated inert shell (NaYF\(_4\)) will block the crucial path of energy dissipation from the core, thus eliminate the concentration quenching effect and lift the optimal doping concentration of Er\(^{3+}\) to 100 mol\%. The time-resolved experimental results re-confirmed our hypothesis. In the bare core, due to the energy dissipation from core to the particle surface, with the Er\(^{3+}\) doping concentration increased from 2 mol\% to 100 mol\%, the decay lifetime of 650 nm emission (\(^4\)F\(_{9/2} \rightarrow \ ^4\)I\(_{15/2}\)) is sharply shortened from 529 \(\mu\)s to 15.9 \(\mu\)s (Figure 3.9c). After the shell coating, the energy dissipation from core to the surface quenching sites is less efficient, resulting in the relatively small change of the decay lifetime (shortened from 562 \(\mu\)s to 311 \(\mu\)s, refer to the Figure 3.9d).

![Diagram](image_url)

**Figure 3.9** The 980 nm excited UC emission spectra of (a) NaYF\(_4\): x\% Er (x: 2-100) bare core, (b) NaYF\(_4\): x\% Er (x: 2-100)@NaYF\(_4\) core-shell nanoparticles (in cyclohexane, normalized by the number of nanoparticles). Insets: Er\(^{3+}\) concentration dependent UC emission intensity (integration from 500 nm to 700 nm) of bare core and core-shell structure, respectively. (c) The decay curves of Er\(^{3+}\): \(^4\)F\(_{9/2} \rightarrow \ ^4\)I\(_{15/2}\) transition (~ 650 nm) in bare core nanostructure and (d) the decay curves of Er\(^{3+}\): \(^4\)F\(_{9/2} \rightarrow \ ^4\)I\(_{15/2}\) transition (~ 650 nm) in core-shell nanostructure.
Figure 3.10 The 800 nm excited UC emission spectra of solutions containing: a) NaYF₄: x% Er (x: 2-100) bare core, b) NaYF₄: x% Er (x: 2-100)@NaYF₄ core-shell nanoparticles in cyclohexane (~1 wt%, 10 W/cm²). Insert in Figure 3.10b: the concentration dependent UC emission intensity (integration from 500 nm to 700 nm) in core-shell structure. And the corresponding decay curves of Er³⁺: ⁴F⁹/₂ → ⁴I₁₅/₂ transition, i.e. ~ 650 nm, in c) NaYF₄: x% Er bare core and d) NaYF₄: x% Er @NaYF₄ core-shell nanoparticles.
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Figure 3.11 The 1530 nm excited UC emission spectra of solutions containing: a) NaYF₄: x% Er (x: 2-100) bare core, b) NaYF₄: x% Er (x: 2-100)@NaYF₄ core-shell nanoparticles in cyclohexane (~1 wt%, 1 W/cm²). Insets in Figure 3.11a,b: the concentration dependent UC emission intensity (integration from 500 nm to 700 nm) of bare core and core-shell structures. And the corresponding decay curves of Er³⁺: ⁴F₉/₂ → ⁴I₁₅/₂ transition, i.e. ~ 650 nm, in c) NaYF₄: x% Er bare core and d) NaYF₄: x% Er@NaYF₄ core-shell nanoparticles.

3.2.3 Potential applications of NaErF₄@NaYF₄ nanostructure

The unique properties of the NaErF₄@NaYF₄ core-shell nanostructures may shed light on many potential applications of UC materials in the fields like biology, display, solar cells and anti-counterfeiting. In the following, two typical applications are performed.

Firstly, we examine its potential in solar energy utilization. In this field, UC materials have the potential to convert NIR to UV/VIS light to enhance the utilization of solar spectrum. Comparing with the traditional co-doping UC materials, the NaErF₄@NaYF₄ nanostructure is privileged to convert three different NIR bands simultaneously rather than only one. More importantly, due to the non-linear relationship exists between excitation power and UC emission intensity (Figure 3.12), the energy convert efficiency will significantly increase when the multi-bands excitation effects are superimposed. Figure 3.13 provides the proof of concept result, where three continuous wave (CW) lasers of 800 nm, 980 nm and 1530 nm were employed so that the
excitation manipulation and beams assembling could be well controlled. For the sake of comparison, the UC emission was recorded under excitation of individual laser. The excitation power of each laser was adjusted to such that the corresponding UC emissions at ~650 nm were comparable in intensity. Then the cooperated excitation of the three lasers was conducted, under cooperated excitation the intensity was 6.1 times higher than that under excitation of individual laser. This result indicates the advantage of this new structure in utilization of solar energy.

**Figure 3.12** Log-log plots of the ~650 nm UC emission intensity of NaErF$_4$@NaYF$_4$ nanoparticles as a function of pump power at (a) 800nm, (b) 980nm and (c) 1530 nm, respectively. The output slopes are measured as 1.82, 1.83 and 1.36, respectively, exhibiting the non-linear relationship between UC emission intensity and excitation power.

**Figure 3.13** Schematic illustration of experimental setup for cooperated excitation with three CW lasers at 800 nm, 980 nm and 1530 nm. And the measured UC emission spectra of NaErF$_4$@NaYF$_4$ nanostructure under 800 nm, 980 nm, 1530 nm and these three CW lasers cooperated excitation, respectively.

On the other hand, the merit of photostability, multi-wavelength excitation, zero-background and anti-stokes emission make the NaErF$_4$@NaYF$_4$ based nanoparticles suitable for anti-counterfeiting. Triply encrypted characters can be achieved by the combination of three types of inks containing different UC materials (Ink I: NaYF$_4$: 20%Yb, 2%Er@NaYF$_4$; 20% Yb@NaYF$_4$:10%Nd; Ink II: NaYF$_4$: 20%Yb, 2%Er@NaYF$_4$; Ink III: NaErF$_4$@NaYF$_4$). As shown in Figure 3.14, the triple encryption was realized by writing concealed information with
different inks layer by layer. Excited with 980 nm, the green characters “8 9 8” from ink I appear to form coding information I. When the excitation wavelength shifts to 800 nm, ink II is excited green characters “4 3 6” appear. By introducing the new material NaErF$_4@$NaYF$_4$ as ink III, the security level is improved. As the excitation is set to 1530 nm, the coding information III displays as red “1 7 5”.

![Figure 3.14](image.png)

**Figure 3.14** (a) Readout under 980 nm, 800 nm and 1530 nm excitation, respectively. (b) Layer by layer preparation of the pattern.

### 3.3 Conclusion

In summary, the concentration quenching effect of Er$^{3+}$ is removed in a core-inert shell structure. This new finding enables us to set up the NaErF$_4@$NaYF$_4$ UC nanostructure and its relevant derivatives (e.g. NaErF$_4$: 0.5% Tm@NaYF$_4$), which successfully achieve three highly desirable UC properties simultaneously, *i.e.* high efficiency (comparable with or even exceeds with ten times the reported optimized traditional nanomaterials), multi-band excitation (~ 800 nm, ~ 980 nm and 1530 nm) and monochromatic red emission. As proof of concept, we have demonstrated the application of this novel nanostructure in solar cell and anti-counterfeiting.
3.4 Experimental details

Reagents. LnCl₃·6H₂O (Ln: Y, Yb, Er >99%), Ln₂O₃ (Ln: Y, Yb, Er, Nd >99%), Oleic acid (OA, 90%), 1-Octadecene (ODE, 90%), Oleylamine (OM, 90%), sodium trifluoroacetate (98%) and trifluoroacetic acid (99%) were purchased from Sigma-Aldrich and used without further purification. NaOH (>98%), NH₄F (>98%), methanol, ethanol and cyclohexane were purchased from GFS Chemical.

Synthesis of 20 nm β-NaYF₄: 20% Yb, 2% Er and 20 nm β-NaYF₄: x% Er (x: 2-100) bare core nanoparticles. The 20 nm β-NaYF₄: Yb, Er nanoparticles and 20 nm β-NaYF₄: x% Er (x: 2-100) nanoparticles were synthesized following a previous literature approach.⁴⁴

Synthesis of the β-core-shell nanoparticles. The NaYF₄: 20% Yb, 2% Er@NaYF₄, NaYF₄: x% Er@NaYF₄ (x:2-100), NaErF₄: 0.5% Tm@NaYF₄ and NaYF₄: 20% Yb, 2% Er@NaYF₄: 20% Yb@NaYF₄: 10% Nd core-shell (or core-shell-shell) nanoparticles were prepared following a previous literature approach.⁴⁵

Characterization. The structure and morphology of the nanoparticles were characterized by using a Brucker D8-advance X-ray diffractometer (XRD) with Cu K-α radiation (λ= 1.5418 Å). The transmission electron microscopy (TEM) was performed on a Tecnai G2 F20 S-TWIN D573 electron microscope operated at 300 kV TEM. Ultraviolet-visible (UV) absorption measurements were recorded using an UV-3101 spectrophotometer. The upconversion emission spectra were measured at room temperature by a Maya 2000 visible spectrometer (Ocean optics). The luminescence dynamics was recorded with a 500 MHz Tektronix digital oscilloscope and the excitation was realized by a nanosecond pulse train at 800 nm, 980 nm and 1530 nm from an optical parametric oscillator.
References


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