



Research Highlight

Realizing efficient ultraviolet emission from Er³⁺-sensitized upconversion nanoparticles under 1550 nm excitation

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Lanthanide-doped upconversion nanoparticles, which enable the conversion of incident low-energy near-infrared (NIR) photons into higher-energy emissions (including NIR, visible, and UV light), have attracted considerable interests because of their promising applications in many fields, such as solar cells, biological imaging, three-dimensional displays, sensors, anti-counterfeiting and therapeutics [1,2]. However, such practical applications are still restricted by the low luminescence efficiency of lanthanide-doped upconversion nanoparticles [3,4]. Concentration quenching is a major limiting factor in developing bright upconversion nanoparticles with optimal luminescence properties [5–7]. In practical, high-doping concentration is required to increase the absorption strength of NIR excitation to improve upconversion efficiency. However, the high-doping concentration will induce additional quenching processes due to the cross-relaxation between dopant ions or energy migration to the surface quenchers, leading to reduction in upconversion efficiency. Thus, it is urgent to find an effective approach to minimize the detrimental concentration quenching effect in highly doped upconversion nanoparticles toward achieving bright luminescence.

The widely used upconversion nanoparticles are commonly doped with Yb³⁺ or Nd³⁺ ions as sensitizers, which absorb the NIR irradiation and nonradiatively transfer their excitation energy to emitting activators (Er³⁺, Tm³⁺, or Ho³⁺) via a two-photon or multi-photon process [8,9]. However, conventional Yb³⁺- and Nd³⁺-sensitized upconversion nanoparticles have considerable limitations, such as fixed excitation bands in the NIR region (980 nm for Yb³⁺ and ~800 nm for Nd³⁺) and very low critical quenching concentrations of activators (below 2 mol%). In sharp contrast, Er³⁺-sensitized upconversion nanoparticles, in which Er³⁺ ions act as both the sensitizer and emitter, can permit high doping concentration of Er³⁺ ions through coating an inert (undoped) shell [7,10]. And more interestingly, the Er³⁺-sensitized upconversion nanoparticles could be efficiently pumped by different visible and NIR wavelengths (650, 808, 980, and 1,532 nm) and exhibited upconverted luminescence with broad wavelength range covering UV, visible and NIR [10–12]. These unique optical properties of Er³⁺-sensitized upconversion nanoparticles offer promising

prospects for designing multi-wavelength-pumped luminescent nanomaterials for particular biomedical or security applications [10,12–16]. However, the mechanism of concentration quenching in Er³⁺-sensitized upconversion nanoparticles is still not clear. Although deleterious cross-relaxation between dopant ions in close proximity and enhanced energy migration via resonant energy transfer to the surface defects (i.e., the surface quenching) have commonly suggested as the two major mechanisms for concentration quenching [7,10], but it is difficult to clarify the contribution of these two mechanisms to the concentration quenching in Er³⁺-sensitized upconversion nanoparticles. And furthermore, previous studies on Er³⁺-sensitized upconversion nanoparticles mainly focus on the visible and NIR upconverted emissions, which belong to the high-order photon upconversion processes (e.g., a two-photon population process for ~650 nm red emission and a three-photon population process for ~540 nm green emission when under 980 nm laser excitation) [10,12]. However, realizing efficient multi-photon-promoted UV upconversion emissions from Er³⁺ ions in Er³⁺-sensitized upconversion nanoparticles has been challenging.

Just recently, reporting in *Nature Communications*, Sun and co-workers [17] proposed an effective strategy to boost the luminescence efficiency of Er³⁺ ions in Er³⁺-sensitized upconversion nanoparticles. The authors realized efficient five-photon UV upconversion luminescence (382 nm) with a large anti-Stokes shift (~1,168 nm) and a high energy conversion efficiency (5%) under 1,550 nm NIR excitation. In this work, Sun and co-workers selected the stoichiometric Er³⁺ compound of NaErF₄ as the host to investigate the Er³⁺-sensitized upconversion luminescence, and they found that the combined use of inert-shell coating and an integrated optical waveguide circuit excitation platform can effectively suppress the concentration quenching effect and thus significantly enhance the upconversion luminescence.

In order to figure out the concentration quenching effect of Er³⁺ ions, Sun and co-workers fabricated a series of NaYF₄:Er (2%–100%) core and the NaYF₄:Er (2%–100%)@NaYF₄ core-shell nanoparticles, and then the authors carried out a systematic and comparative study on concentration-dependent decay dynamics for Er³⁺ ions in these nanoparticles under 1,532 nm excitation with same pump power density. In NaYF₄:Er core nanoparticles, the decay lifetimes

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of several excited states ($^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$) were shortened at high doping concentrations due to the concentration quenching. In sharp contrast, the $\text{NaYF}_4:\text{Er}@\text{NaYF}_4$ core-shell counterparts had much longer lifetimes because of the significant suppression of concentration quenching via inert-shell coating. Moreover, the authors observed that in $\text{NaYF}_4:\text{Er}@\text{NaYF}_4$ core-shell nanoparticles, the dependence of decay lifetime on Er^{3+} concentration was not uniform for different excited states. With increasing Er^{3+} concentration in $\text{NaYF}_4:\text{Er}@\text{NaYF}_4$ core-shell nanoparticles, the lifetimes of $^4I_{11/2}$ and $^4I_{13/2}$ states almost kept the same, whereas the $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{9/2}$ states exhibited faster decay times for high doping concentrations. Consequently, the authors revealed that in $\text{NaErF}_4@\text{NaYF}_4$ core-shell nanoparticles the concentration quenching of individual excited state of Er^{3+} ions was dominated by different processes (Fig. 1a). The energy migration to quenching centers was the major mechanism responsible for the concentration quenching of $^4I_{11/2}$ and $^4I_{13/2}$ states at high doping level, whereas the cross-relaxation and phonon-assisted energy transfer mainly resulted in the concentration quenching of the $^4S_{3/2}$, $^4F_{9/2}$, and $^4I_{9/2}$ states. Accordingly, the use of core-shell nanostructure alone can effectively suppress the surface quenching effect, but it cannot mitigate the concentration quenching due to cross-relaxation and phonon-assisted energy transfer. As a result, under 1,532 nm excitation, the $\text{NaErF}_4@\text{NaYF}_4$ core-shell nanoparticles showed bright red emission at 658 nm ($^4F_{9/2} \rightarrow ^4I_{15/2}$ transition), but very weak UV emission at 382 nm ($^4G_{11/2} \rightarrow ^4I_{15/2}$ transition) was observed (Fig. 1b).

To further significantly reduce the concentration quenching, Sun and co-workers first demonstrated a novel approach to greatly enhance the upconversion luminescence of $\text{NaErF}_4@\text{NaYF}_4$ core-shell nanoparticles, by using an optical microring resonator excitation platform (Fig. 1c). The integrated waveguide circuit could improve the interaction length between the excitation photons

with the nanoparticles and thus increase the absorption of NIR excitation. The authors putted the upconversion nanoparticles on the surface of the waveguide substrate, and these nanoparticles can be excited by evanescent fields of the waveguides. More interestingly, the input excitation on/off resonance of the resonator could be easily tuned by a tunable continuous-wave laser, and the on-resonance status affords a much stronger electric field than that in the straight waveguide (off-resonance). Notably, the authors found that for a 20 mW input pump power, the microring resonator provided a highly amplified excitation density compared to the straight bus waveguide (2,300 versus 133 kW/cm^2). Consequently, intense UV upconversion emission with energy conversion efficiency of 5% was achieved when the resonance status was changed by tuning the wavelength of incident light from 1,550.00 nm (off-resonance) to 1,549.47 nm (on-resonance), due to effective alleviation of concentration quenching (Fig. 1d). High dopant concentrations are crucial to realize bright UV upconversion (Fig. 1e), which could be attributed to a combination of increased absorption of NIR irradiance and accelerated energy transfer between adjacent Er^{3+} ions. One unique feature of this proposed integrated optical waveguide circuit excitation platform is that it can offer desirable amplified excitation to upconversion particles without the requirement for controlling their assembly on the waveguide. What's more, these intense upconverted UV emissions can be used for precise formation of polymer waveguides and periodic patterns.

Overall, the work presented by Sun and co-workers not only sheds light on the concentration quenching mechanism of lanthanide-doped upconversion nanoparticles, but also provides new insights for rational design of high-efficiency upconverting nanomaterials for promoting their sooner practical applications in many important fields. The strategy for boosting the upconversion luminescence of Er^{3+} ions proposed by Sun and co-workers

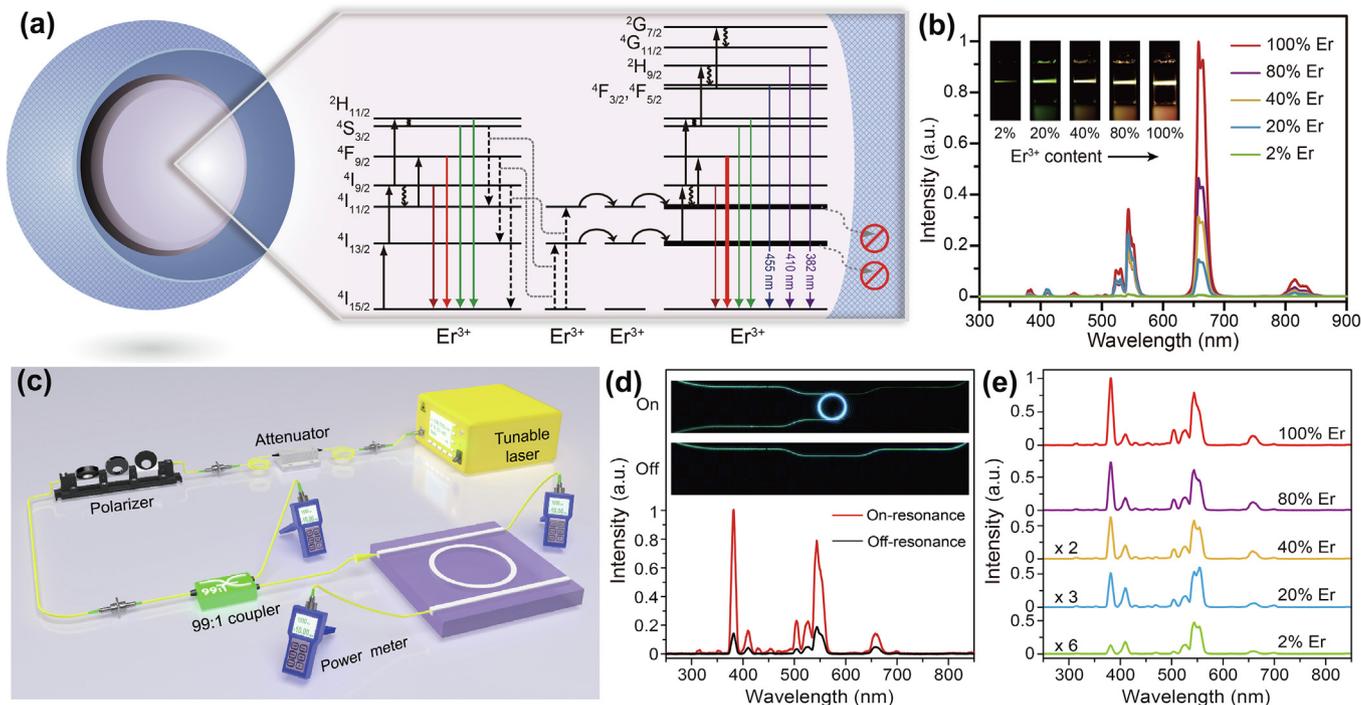


Fig. 1. (Color online) Concentration quenching in the $\text{NaYF}_4:\text{Er}@\text{NaYF}_4$ nanocrystals and microring resonator-assisted excitation of $\text{NaErF}_4@\text{NaYF}_4$ nanocrystals. (a) Proposed concentration quenching processes in $\text{NaErF}_4@\text{NaYF}_4$ core-shell nanoparticles by 1,532 nm excitation. (b) Emission spectra of $\text{NaYF}_4:\text{Er}$ (2%–100%)@ NaYF_4 nanoparticles as a function of Er^{3+} concentration under excitation of a 1,532 nm continuous-wave diode laser (power density: 21 W/cm^2). (c) Schematic diagram of the set-up for the microring resonator-assisted excitation scheme. (d) Emission spectra and optical micrographs (inset) recorded from an identical specimen in different resonance states. (e) Emission spectra of $\text{NaYF}_4:\text{Er}$ (2%–100%)@ NaYF_4 nanoparticles as a function of Er^{3+} concentration under microring resonator-assisted excitation (1,549.47 nm, 2,300 kW/cm^2). Adapted with permission from Ref. [17], Copyright (2019) Springer Nature.

might be extended to other lanthanide-doped upconversion nanoparticle systems. These findings open new opportunities for realizing bright upconverted UV light sources towards various optoelectronic and photonic applications.

Conflict of interest

The author declares that he has no conflict of interest.

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Xiaoyong Huang obtained his Ph.D. degree from South China University of Technology in 2011. Afterwards, he worked as postdoctoral researcher at the National University of Singapore. His current research mainly focuses on the design, synthesis and characterization of functional materials towards applications in photonic and optoelectronic devices, sensors, and photocatalysis.