

Original Research Paper

A General Strategy to Enhance Upconversion luminescence in Rare-Earth-Ion-Doped Oxide Nanocrystals

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Abstract: We report a general strategy to enhance upconversion luminescence from rare-earth-doped oxide nanocrystals through tailoring the local crystal field around rare earth ions. We show that upconversion luminescence from oxide nanocrystals of various host lattice (Y_2O_3 , Gd_2O_3 and ZnO) and of diverse rare-earth-ions (such as Er^{3+} , $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Ho}^{3+}$ and $\text{Yb}^{3+}/\text{Tm}^{3+}$) was enhanced by orders of magnitude through an introduction of non-luminescent Li^+ ions into the lattice. These oxide nanocrystals with tailored upconversion luminescence are able to evoke higher photoluminescence from organic dye molecules, posing their potential use in photodynamic therapy of deep tumors.

Keywords: Upconversion, Enhancement, Rare-Earth, Oxide Nanocrystals

Introduction

Inorganic Upconversion (UC) nanocrystals doped with rare-earth ions have garnered significant attentions in literature due to their potential use in color displays (Shalav *et al.*, 2005), solar cells (Liu *et al.*, 2004), DNA detection (Wang and Li, 2006), background-free fluorescence imaging (Lim *et al.*, 2006) and deep tumor treatment via Photodynamic Therapy (PDT) (Chen *et al.*, 2014), etc. Such endeavors gain a lot from UC nanocrystals' unique capability that they can upconvert the absorbed, usually infrared and Near Infrared (NIR) light, into visible and ultraviolet radiations via the embedded rare-earth ions (Auzel, 2004; Vetrone *et al.*, 2003). Unfortunately, these nanocrystals display a serious shortcoming, since their luminescent efficiency is inadequate to meet the requirements of many practical applications (Suyver *et al.*, 2005; Sivakumar *et al.*, 2007). Among inorganic nanocrystals, oxide nanocrystals exhibit higher mechanical, thermal and chemical stabilities and constitute a distinguished endeavor for biomedical and photonic applications. The realization of efficient NIR to visible UC Luminescence (UCL) in the category of oxide nanocrystals will unlock a realm of new possibilities for their biomedical and photonic applications.

It is known that the main intra-4f electronic-dipole transitions of rare-earth ions are forbidden by the quantum mechanical selection rules. However, this prohibited nature can be broken by the rare-earth ions' local surrounding crystal field due to its capability to intermix the f states of rare earth ions with the higher electronic

configurations (Weber, 1967). We thereby propose a strategy on engineering on rare-earth ions' local environment in the host lattice to tailor their radiation parameters to increase the UCL output. The Li^+ ions have the smallest cationic radius in the periodic table (favorable for the movement and localization in the lattice) that makes them attractive for use in this task. The Li^+ ions around rare-earth ions in the lattice, particularly that occupy the interstitial sites, can impose a columbic field on rare earth ions, which thereby can modify the local environment to increase the UCL. Based on this hypothesis, we have demonstrated that the UCL from $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ nanocrystals can be significantly increased via codoping with Li^+ ions (Chen *et al.*, 2008a). Bai *et al.* (2008) reported on a similar observation in parallel. Here, we generalize this strategy to the category of oxide nanocrystals and to the class of rare-earth ions. Measured experimental results evidenced that the UCL could be increased by orders of magnitude via doping further with Li^+ ions. Regarding the generalization of the proposed strategy, we took two parallel steps to justify the conclusion: (1) the demonstration of its general validity in nanocrystals of different oxide host lattice doped with a specific rare-earth ion; (2) the demonstration of its general validity for diverse rare-earth ions (codoping and tridoping) in a specific host lattice.

Experimental

Nanocrystals of Y_2O_3 (Gd_2O_3 or ZnO) powders doped with Er^{3+} ($\text{Yb}^{3+}/\text{Tm}^{3+}$, $\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Yb}^{3+}/\text{Ho}^{3+}$ and

$\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$) and codoped with various concentrations of Li^+ ion were synthesized according the following procedure: Yttrium nitrate, rare-earth nitrates (Er^{3+} , Tm^{3+} , Ho^{3+} and Yb^{3+}) and lithium nitrate, with corresponding mole ratio, were first completely dissolved in the deionized water. Subsequently, citric acid was added into the solution with a mole ratio of (Y+RE+Li) to citric acid of 1:4. After complete dissolution, the pH of the solution was adjusted to 6.0 by addition of ammonium hydroxide. The resulting solution was dried at 120°C for 24 h until it was transformed into a black bulk, which was further calcined at 800°C for 2 h in air. The bulk ceramic $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ 1 mol% was achieved by sintering the corresponding pressed powder disk (made of nanocrystals $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ 1 mol%) in a tubular furnace at 1300°C for 24 h in air. Further, the powders were pressed to form smooth and flat disks to be utilized for spectral studies by irradiation with a focused 976 nm diode laser (Hi-Tech Optoelectronics Co. Ltd, Beijing) at an output of 400 mW. The focus area on the disk sample was measured to be about 1 mm², resulting in a power density of about 40 W/cm². The emitted UCL was collected by a lens-coupled monochromator (Zolix Instruments Co. Ltd, Beijing) of 2-nm spectral resolution with an attached photomultiplier tube (Hamamatsu R928). All spectral measurements were performed at room temperature and preserving the same geometry for the UCL recording. X-ray diffraction patterns evidenced that the prepared powders were about 60 nm in diameter and there was no crystal structure changes for all these oxide nanocrystals via doping further with Li^+ ions. The morphology of these rare-earth-doped nanocrystals are similar to that in our previous reports (Chen *et al.*, 2008b).

Results

Figures 1a-c present the green UCL from Y_2O_3 and Gd_2O_3 nanocrystals doped with 1 mol% Er^{3+} ions and codoped with various Li^+ ions and from ZnO nanocrystals doped with 2 mol% Er^{3+} ions and codoped with various Li^+ ions under 976 nm diode laser excitation of about 40 W/cm². These emissions were identified to arise from the intra-4f electronic transition $^2\text{H}_{11/2}/^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ of the Er^{3+} ions. As shown in these figures, codoping with Li^+ ions can remarkably enhance the green UCL in all these oxide nanocrystals. The green UCL are enhanced up to about 70, 33 and 35 times in Y_2O_3 , Gd_2O_3 and ZnO nanocrystals when codoped with Li^+ ions of 5, 5 and 2 mol%, respectively. The intensity of green UCL in nanocrystals of Y_2O_3 codoped with 5 mol% Li^+ ions can even reach one third of the one from the bulk counterpart (Fig. 1d), which means that such enhancement strategy enables UC nanocrystals to radiate like bulk materials. It is worthwhile to point out

that ever since the first report by F. Auzel in the 1960s on UC enhancement through Yb^{3+} sensitization (Auzel, 2004), there have been limited strategies to increase the UCL by orders of magnitude. The significant UCL enhancements in various oxide nanocrystals illustrate well the general validity of the proposed strategy for different oxide host lattice.

Among rare-earth ions, the activators of Tm^{3+} , Er^{3+} and Ho^{3+} ions sensitized by Yb^{3+} ions have been reported to be the most efficient UC systems in the literature (Auzel, 2004; Chen *et al.*, 2014). Hence, we select them here as a model to demonstrate the general validity of the proposed strategy for the category of rare-earth ions. Figure 2 contrasts the UCL spectra of (a) single blue ($^1\text{G}_4 \rightarrow ^3\text{H}_6$) of Tm^{3+} ions in nanocrystals $\text{Y}_2\text{O}_3:\text{Yb}^{3+}/\text{Tm}^{3+}$ tridoped without and with Li^+ ions, (b) single green ($^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$) of Ho^{3+} ions in nanocrystals $\text{Y}_2\text{O}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ tridoped without and with Li^+ ions and (c) single red ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{5/2}$) of Er^{3+} ions in nanocrystals $\text{Y}_2\text{O}_3:\text{Yb}^{3+}/\text{Er}^{3+}$ tridoped without and with Li^+ ions. As expected, magnificent fluorescence increases (by one order of magnitude) were observed for all these types of rare-earth ions via tridoping with Li^+ ions. It should be noted that these achieved highly luminescent single-band UCL are of interest for background-free multicolor imaging and for simultaneous parallel quantitative analysis of multiple biological species. These achieved significant UCL enhancements in diverse rare-earth ions (codoping and tridoping) illustrate well the general validity of the proposed strategy for the class of rare-earth ions.

Discussion

Mechanisms for the UCL enhancement in Er^{3+} -doped oxide nanocrystal (Y_2O_3 , Gd_2O_3 and ZnO), as discussed in our previous report (Chen *et al.*, 2008a), arise from the fact that the codoping of Li^+ ions can tailor the local crystal field around the Er^{3+} ions. The tailored local crystal field will interact with Er^{3+} ion, slightly modify its wave functions and eventually alter the radiation parameters of the intermediate $^4\text{I}_{11/2}$ state and lead the UCL to increase by orders of magnitude. The same enhancement mechanism is expected for all these Er^{3+} -doped oxide nanocrystals due to the fact that Li^+ ions have similar effects on the nanocrystal size, lattice structure, intensity ratio of the green to red UC emission and enhancement outcomes. Else, mechanisms for UCL enhancement in $\text{Yb}^{3+}/\text{Tm}^{3+}$, $\text{Yb}^{3+}/\text{Ho}^{3+}$ and $\text{Yb}^{3+}/\text{Er}^{3+}$ ions, may arise from the fact that the tridoping with Li^+ ions can tailor both the lifetime of the excited $^2\text{F}_{5/2}$ state in Yb^{3+} ions and the lifetime of the intermediate states in Tm^{3+} , Ho^{3+} and Er^{3+} ions. This is because that the sensitization of Yb^{3+} ions and the tailoring lifetime of rare-earth ions are two independent enhancement mechanisms for the UCL output (Chen *et al.*, 2008b).

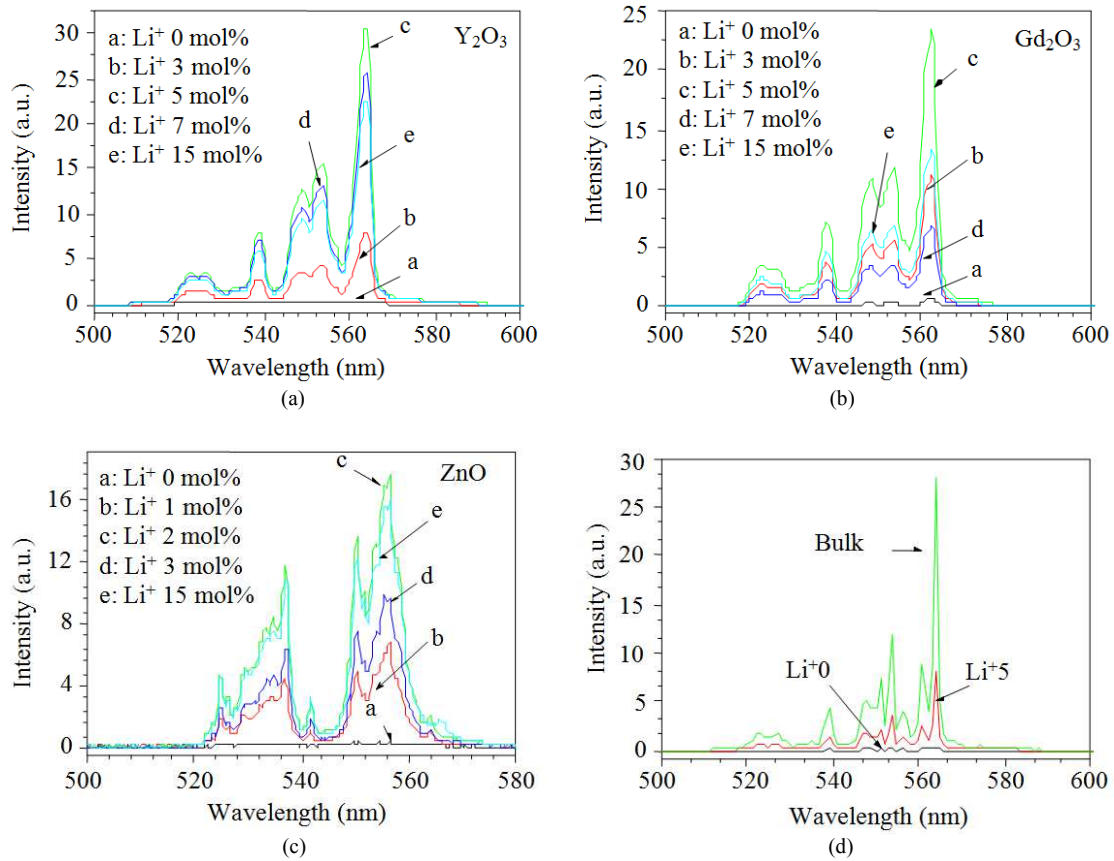


Fig. 1. Measured UCL of (a) Y₂O₃:Er³⁺ 1 mol% nanocrystals, (b) Gd₂O₃:Er³⁺ 1 mol% nanocrystals, (c) ZnO:Er³⁺ 2 mol% nanocrystals codoped with various Li⁺ ions under 976 nm diode laser excitation of 40 W/cm²; (d) Contrasted UC spectra of nanocrystals and bulk Y₂O₃:Er³⁺ 1 mol%, as well as nanocrystals Y₂O₃ doped further with 5 mol% Li⁺ ions

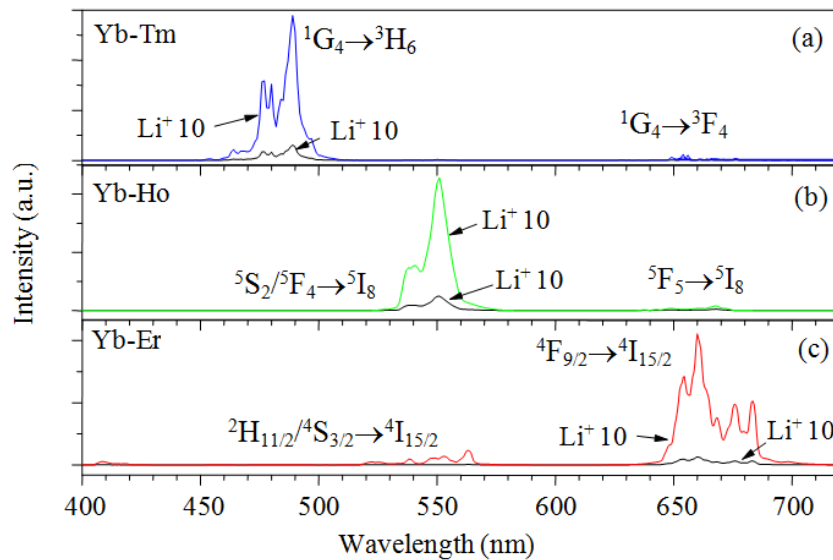


Fig. 2. Contrasted UCL spectra of the (a) single blue in nanocrystals Y₂O₃ doped with 3 mol% Yb³⁺, 0.2 mol% Tm³⁺ ions and nanocrystals Y₂O₃ doped further with 15 mol% Li⁺ ions, (b) single green in nanocrystals Y₂O₃ doped with 2 mol% Yb³⁺, 1 mol% Ho³⁺ ions and nanocrystals Y₂O₃ doped further with 10 mol% Li⁺ ions; and (c) single red in nanocrystals Y₂O₃ doped with 10 mol% Yb³⁺, 1 mol% Er³⁺ ions and nanocrystals Y₂O₃ doped further with 10 mol% Li⁺ ions

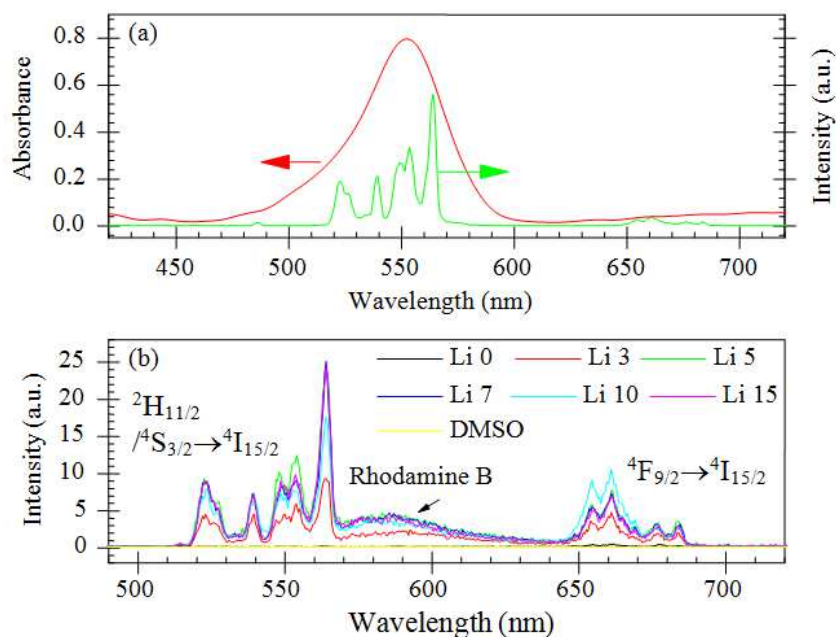


Fig. 3. (a) The absorbance of Rhodamine B and the UCL spectrum from colloidal Y₂O₃:Er³⁺ 1 mol% nanocrystals in DMSO solution with different scales marked by the arrows in the figure; (b) visible fluorescence of DMSO solutions containing Rhodamine B and Y₂O₃:Er³⁺ 1 mol% nanocrystals doped with various Li⁺ ions under diode laser excitation of 976 nm

As a proof-of-principle, a model PDT experiment was implemented by pumping Y₂O₃:Er³⁺ nanocrystals with 976 nm diode laser for UC-mediated resonant (Fig. 3a) excitation of organic Rhodamine B molecules dissolved in a DMSO solution. The fluorescence of the organic dye-here acting as ad hoc photosensitizer-can reflect the output of ¹O₂, which has the direct task to destroy the tumor cells. The three peaks in Fig. 3b centered around 560, 590 and 660 nm can easily be assigned to the green UC emission, the Rhodamine B fluorescence and the red UC emission, respectively. The fluorescence of Rhodamine B in DMSO solutions containing Y₂O₃ nanocrystals doped only with Er³⁺ ions is too weak to be displayed. In contrast, the fluorescence of Rhodamine B in solution with Y₂O₃:Er³⁺ 1 mol% nanocrystals codoped with Li⁺ ions can be clearly observed and their intensities follow the same tendency as that of Fig. 1a. As demonstrated, the significant fluorescence increase in UC nanocrystals can expectedly result in a great enhancement of the fluorescent signal in organic dyes, these being potential photosensitizers in PDT and thereby increasing the output of ¹O₂.

Conclusion

In summary, we have demonstrated a general strategy to increase the UCL by orders of magnitude via non-luminescent Li⁺ ions doping in rare-earth-ion-doped oxide nanocrystals, such as Y₂O₃, Gd₂O₃ and ZnO doped with Er³⁺, Yb³⁺/Er³⁺, Yb³⁺/Ho³⁺ and Yb³⁺/Tm³⁺. The

achieved UCL, for example, in Li⁺-codoped Y₂O₃:Er³⁺ nanocrystals can even be comparable to that of the bulk counterpart. Such enhancement mainly arises from the modification of rare-earth ions' local environment by Li⁺ ions doping. A proof-of-principle PDT experiment targeting treatment of deep tumors suggests the advantage of significantly increased UCL for various photonic and biomedical applications.

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Author's Contributions

Guanying Chen: Developed the idea, performed the experiments, analyzed the data and wrote the manuscript.

Lei Xu: Performed some of the experiments.

Ethics

We would like to disclose that Dr. Guanying Chen is an Associate Editor for the American Journal of Engineering and Applied Sciences.

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