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

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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 cites, can impose a cumbic field 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 cites, can impose a cumbic field 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 cites, can impose a cumbic field 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 cites, can impose a cumbic field for the movement and localization in the lattice (that makes them attractive for use in this task).

Abstract: We report a general strategy to enhance upconversion luminescence from rare-earth-doped oxide nanocrystals through tailoring the local crystal filed around rare earth ions. We show that upconversion luminescence from oxide nanocrystals of various host lattice (Y₂O₃, Gd₂O₃ and ZnO) and of diverse rare-earth-ions (such as Er³⁺, Yb³⁺/Er³⁺, Yb³⁺/Ho³⁺ and Yb³⁺/Tm³⁺) 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

Experimental

Nanocrystals of Y₂O₃ (Gd₂O₃ or ZnO) powders doped with Er³⁺ (Yb³⁺/Tm³⁺, Yb³⁺/Er³⁺, Yb³⁺/Ho³⁺ and
Yb\(^{3+}\)/Er\(^{3+}/\)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. The bulk ceramic Y\(_2\)O\(_3\):Er\(^{3+}\) 1 mol% was achieved by sintering the corresponding pressed powder disk (made of nanocrystals Y\(_2\)O\(_3\)) utilized for spectral studies by irradiation with a 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 mm\(^2\), resulting in a power density of about 40 W/cm\(^2\). 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\(_2\)O\(_3\) and Gd\(_2\)O\(_3\) 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/cm\(^2\). These emissions were identified to arise from the intra-4f electronic transition \(^{3}\)H\(_{11/2}\)/\(^{4}\)S\(_{3/2}\)→\(^{1}\)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\(_2\)O\(_3\), Gd\(_2\)O\(_3\) and ZnO nanocrystals when codoped with Li\(^+\) ions of 5, 5 and 2 mol\%, respectively. The intensity of green UCL in nanocrystals of Y\(_2\)O\(_3\) 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\(^{3+}\), 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 (\(^{5}\)G\(_{4}\)→\(^{7}\)H\(_{6}\)) of Tm\(^{3+}\) ions in nanocrystals Y\(_2\)O\(_3\):Yb\(^{3+}/\)Tm\(^{3+}\) tridoped without and with Li\(^+\) ions, (b) single green (\(^{5}\)S\(_{2}\)→\(^{3}\)I\(_{1}\)) of Ho\(^{3+}\) ions in nanocrystals Y\(_2\)O\(_3\):Yb\(^{3+}/\)Ho\(^{3+}\) tridoped without and with Li\(^+\) ions and (c) single red (\(^{5}\)F\(_{9/2}\)→\(^{3}\)I\(_{15/2}\)) of Er\(^{3+}\) ions in nanocrystals Y\(_2\)O\(_3\):Yb\(^{3+}/\)Er\(^{3+}\) tridoped without and with Li\(^+\) ions. As expected, magnitude 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\(_2\)O\(_3\), Gd\(_2\)O\(_3\) 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 \(^{3}\)I\(_{15/2}\) 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 Yb\(^{3+}/\)Tm\(^{3+}\), Yb\(^{3+}/\)Ho\(^{3+}\) and Yb\(^{3+}/\)Er\(^{3+}\) ions, may arise from the fact that the tridoping with Li\(^+\) ions can tailor both the lifetime of the excited \(^{5}\)F\(_{9/2}\) 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) Y$_2$O$_3$:Er$^{3+}$ 1 mol% nanocrystals, (b) Gd$_2$O$_3$:Er$^{3+}$ 1 mol% nanocrystals, (c) ZnO:Er$^{3+}$ 2 mol% nanocrystals codoped with various Li$^+$ ions under 976 nm diode laser excitation of 40 W/cm$^2$; (d) Constrained UC spectra of nanocrystals and bulk Y$_2$O$_3$:Er$^{3+}$ 1 mol%, as well as nanocrystals Y$_2$O$_3$ doped further with 5 mol% Li$^+$ ions.

Fig. 2. Contrasted UCL spectra of the (a) single blue in nanocrystals Y$_2$O$_3$ doped with 3 mol% Yb$^{3+}$, 0.2 mol% Tm$^{3+}$ ions and nanocrystals Y$_2$O$_3$ doped further with 15 mol% Li$^+$ ions, (b) single green in nanocrystals Y$_2$O$_3$ doped with 2 mol% Yb$^{3+}$, 1 mol% Ho$^{3+}$ ions and nanocrystals Y$_2$O$_3$ doped further with 10 mol% Li$^+$ ions; and (c) single red in nanocrystals Y$_2$O$_3$ doped with 10 mol% Yb$^{3+}$, 1 mol% Er$^{3+}$ ions and nanocrystals Y$_2$O$_3$ doped further with 10 mol% Li$^+$ ions.
Fig. 3. (a) The absorbance of Rhodamine B and the UCL spectrum from colloidal Y$_2$O$_3$:Er$^{3+}$ 1 mol% nanocrystals in DMSO solution with different scales marked by the arrows in the figure; (b) visible fluorescence of DMSO solutions containing Rodamine B and Y$_2$O$_3$:Er$^{3+}$ 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 Y$_2$O$_3$:Er$^{3+}$ 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 $^{18}$O$_2$, 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 Y$_2$O$_3$ nanocrystals doped only with Er$^{3+}$ ions is too weak to be displayed. In contrast, the fluorescence of Rhodamine B in solution with Y$_2$O$_3$:Er$^{3+}$ 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 $^{18}$O$_2$.

**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 Y$_2$O$_3$, Gd$_2$O$_3$ and ZnO doped with Er$^{3+}$, Yb$^{3+}$/Er$^{3+}$, Yb$^{3+}$/Ho$^{3+}$ and Yb$^{3+}$/Tm$^{3+}$. The achieved UCL, for example, in Li$^+$-codoped Y$_2$O$_3$:Er$^{3+}$ 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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