RSC Advances

PAPER

Cite this: *RSC Adv.*, 2016, **6**, 3440

# Enhancing up-conversion luminescence of $Er^{3+}$/$Yb^{3+}$-codoped glass by two-color laser field excitation

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Improving up-conversion luminescence efficiency of rare-earth ions is always a research hotspot because of its important applications in laser source, color display, photoelectric conversion and multiplexed biolabeling. Herein, we first utilize a combined two-color laser field with the laser wavelengths of 800 and 980 nm to further enhance the up-conversion luminescence in an $Er^{3+}$/$Yb^{3+}$-codoped glass sample. We show that the green up-conversion luminescence intensity by the combined two-color laser field can be greatly enhanced by comparing it with the sum of that induced by the two individual laser fields. We also show that the luminescence enhancement can be attributed to the cooperative up-conversion excitation process by the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions *via* the 980 nm laser field excitation and then the excited state absorption *via* the 800 nm laser field excitation. These studies present a clear physical picture for the up-conversion luminescence generation and enhancement in an $Er^{3+}$/$Yb^{3+}$-codoped glass sample, which are very helpful for properly designing the laser field to generate or improve the up-conversion luminescence efficiency in various lanthanide-codoped luminescent materials.

Received 7th November 2015
Accepted 16th December 2015

DOI: 10.1039/c5ra23464f

www.rsc.org/advances

## 1. Introduction

The up-conversion luminescence by converting the low-frequency stimulation into high-frequency emission in lanthanide-doped luminescent materials has attracted wide interest over the past twenty years. Usually, there are four main formation mechanisms in the up-conversion luminescent process, which include the excited state absorption (ESA),[1,2] energy transfer up-conversion (ETU),[3] multi-photon absorption (MPA)[4,5] and photon avalanche (PA).[6,7] Because of many unique properties, such as the narrow emission spectrum, abundant energy levels, high conversion efficiency and good optical stability, the lanthanide-doped luminescent materials have been widely applied in various related fields, for example, laser source,[8,9] fiber optical communication,[10,11] color display,[12–14] medical imaging,[15,16] and biological labels.[17,18] To further extend the related applications of the lanthanide-doped luminescent materials, it is necessary to improve the up-conversion luminescence efficiency as much as possible. To date several methods have been proposed and experimentally realized, such as changing the doped concentration of rare-earth ions,[19–21] selecting the dopant–host combination,[22–24] adding the co-doping ions,[25] varying the excitation wavelength,[26] controlling the repetition rate and pulse duration of the excitation laser,[27,28] utilizing the two- or multi-wavelength excitation,[29–31] manipulating the excitation pulse shape,[32–35] and applying the electric field or magnetic field on the luminescent materials.[36,37]

$Er^{3+}$/$Yb^{3+}$-codoped glass, as one of the most commonly used luminescent materials, has attracted considerable attention, but methods to improve its up-conversion luminescence efficiency are always a focus for scientists. The host matrix has a great effect on the luminescence efficiency, and thus the $Er^{3+}$/$Yb^{3+}$-codoped glasses with different host materials have been widely studied, such as germanate,[38] tellurite,[39] phosphate,[40] aluminate,[41] and oxyfluoride glasses.[42] Generally, the host materials with lower phonon energy are beneficial for the luminescence efficiency, because the higher phonon energy will lead to the higher non-radiative relaxation probability, which will limit the luminescence efficiency. Furthermore, the concentration of $Er^{3+}$ or $Yb^{3+}$ ions is also an important factor for the up-conversion luminescence efficiency because of the concentration quench, and therefore the optimal concentrations in different $Er^{3+}$/$Yb^{3+}$-codoped glass samples have been systematically investigated.[43,44] In this study, we first propose a combined two-color laser field with the laser wavelengths of 800 and 980 nm to further enhance the up-conversion luminescence intensity in an $Er^{3+}$/$Yb^{3+}$-codoped glass sample. Our experimental results show that, compared with the two

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individual laser field excitations, the combined two-color laser field excitation can greatly improve the up-conversion luminescence efficiency, the cooperative up-conversion excitation process by the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions *via* the 980 nm laser field excitation and then the excited state absorption *via* the 800 nm laser field excitation. This is identified as the luminescence enhancement mechanism. One important advantage for the two-color laser field excitation is that the up-conversion luminescence efficiency can be further improved in a single material, which is different from previous studies that involve varying the material property, where the preparation of a series of materials is needed.[19–25] Moreover, these studies can provide a way to understand and control the up-conversion luminescent process in lanthanide/$Yb^{3+}$-codoped luminescent materials, and the cooperative up-conversion excitation strategy can also open a new opportunity for the related applications of lanthanide-codoped luminescent materials.

## 2. Experimental arrangement

Our experimental arrangement is shown in Fig. 1, where a fiber laser (Connet, VLSS-980-B-F-600) provides the near-infrared (980 nm) continuous-wave output, and a Ti-sapphire laser (Spectra-Physics, Tsunami) provides the near-infrared (800 nm) continuous-wave output. Two attenuators are respectively used to vary the output intensities of the two lasers, and finally the two lasers are focused into the sample from opposite directions using two lenses with the focal length of 300 mm. All the luminescence signals emitted from the sample are perpendicularly collected by a lens, and measured by a spectrometer with a charge-coupled device (CCD).

The sample used in our experiment is a piece of glass containing the rare-earth ions $Er^{3+}$ and $Yb^{3+}$, which is synthesized *via* modification from melt-quenching to subsequent heat treatment, as shown in the inset of Fig. 1. One can see that our glass sample has a higher transparency. The precursor sample is prepared with the composition (in mol%) of 40% $SiO_2$, 25% $Al_2O_3$, 18% $Na_2CO_3$, 10% $YF_3$, 7% NaF, 0.25% $ErF_3$, and 1% $YbF_3$. The starting materials were mixed and melted in a covered platinum crucible at a temperature of 1450 °C for 45 minutes in ambient atmosphere and then cast into a brass mold followed by annealing at the temperature of 450 °C for 10 hours. Finally, the glass sample is cut and polished for optical measurement in our experiment.

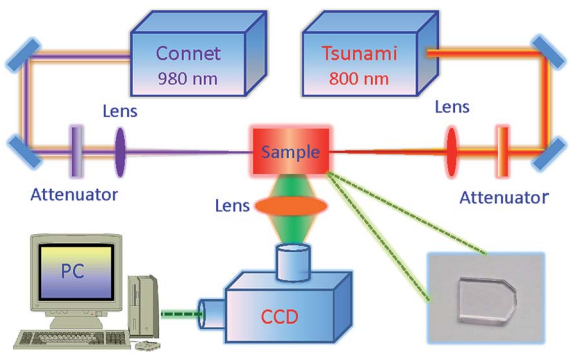


Fig. 1 The schematic diagram of the experimental arrangement for the two-color laser field excitation in the $Er^{3+}/Yb^{3+}$-codoped glass sample. Here, the glass sample picture is shown in the inset.

## 3. Results and discussion

The VIS-NIR absorption spectrum of the $Er^{3+}/Yb^{3+}$-codoped glass sample was obtained by a U-4100 spectrophotometer (Hitachi), and the result is shown in Fig. 2(a), where the absorption peaks are mainly distributed at 408, 482, 520, 556, 647, 798 and 980 nm, and these absorption peaks at 408, 482, 520, 556, 647 and 798 nm can be attributed to the state transitions from the ground state $^4I_{15/2}$ to the $^2H_{9/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$ and $^4I_{9/2}$ excited states of $Er^{3+}$ ions, but the absorption peak at 980 nm should be attributed to both the state transitions from the ground state $^4I_{15/2}$ to the excited state $^4I_{11/2}$ of $Er^{3+}$ ions and the ground state $^2F_{7/2}$ to the excited state $^2F_{5/2}$ of $Yb^{3+}$ ions. The up-conversion luminescence spectra of the $Er^{3+}/Yb^{3+}$-codoped glass sample under the excitations of the 800 nm Tsunami and 980 nm Connet laser fields are shown in Fig. 2(b). For the case of the 800 nm Tsunami laser field excitation, the main up-conversion luminescence peaks are observed at 525 and 547 nm, called green up-conversion luminescence, which is due to the state transitions from the two excited states $^2H_{11/2}$ and $^4S_{3/2}$ to the ground state $^4I_{15/2}$, while for the case of the 980 nm Connet laser field excitation, the up-conversion luminescence peak at 656 nm is also observed in addition to the two peaks at 525 and 547 nm, and called as the red up-conversion luminescence; this results from the state transition from the excited state $^4F_{9/2}$ to the ground state $^4I_{15/2}$. In other words, when the $Er^{3+}/Yb^{3+}$-codoped glass sample is excited by the 800 nm Tsunami laser field, only the green up-conversion luminescence can be emitted, while when excited by the 980 nm Connet laser field, both the green and red up-conversion luminescence can be emitted.

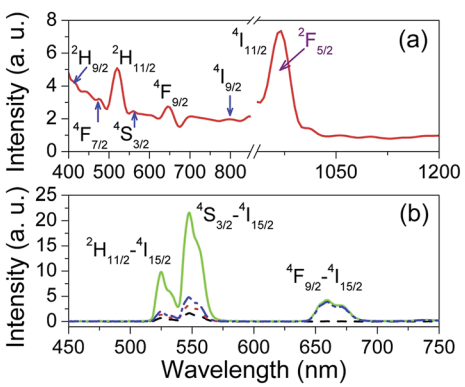


Fig. 2 The VIS-NIR absorption (a) and up-conversion luminescence (b) spectra of $Er^{3+}/Yb^{3+}$-codoped glass sample. Here, the black dashed line, red dotted line and green solid line are used to show the luminescence spectra excited by the 800 nm Tsunami laser field, 980 nm Connet laser field and their combined laser field, respectively. The blue dash-dotted line represents the sum of the luminescence spectra excited by the two individual laser fields.

As shown in Fig. 2(b), when the $Er^{3+}/Yb^{3+}$-codoped glass sample is simultaneously excited by the 800 nm Tsunami and 980 nm Connet laser fields, both the green and red up-conversion luminescence can be clearly observed, but a more interesting phenomenon is that the green up-conversion luminescence intensity by the combined two-color laser field excitation is far larger than the sum of that individually excited by the 800 nm Tsunami and 980 nm Connet laser fields. Therefore, the green up-conversion luminescence enhancement can be achieved by the two-color laser field excitation strategy, and the enhancement efficiency can be up to about 6. However, the red up-conversion luminescence intensity is almost negligibly enhanced, which is different from the green up-conversion luminescence. Consequently, one can also realize the red and green up-conversion luminescence tuning by properly controlling both the 800 nm Tsunami and 980 Connet laser intensities.

To further study the green up-conversion luminescence enhancement in the $Er^{3+}/Yb^{3+}$-codoped glass sample by the two-color laser field excitation, we measure the green up-conversion luminescence intensity by varying one laser intensity while the other laser intensity is fixed, and the experimental results are shown in Fig. 3. We can see that, when the 980 nm Connet laser intensity is fixed at 20 W $cm^{-2}$, the green up-conversion luminescence intensity will increase with the increase in the 800 nm Tsunami laser intensity, and the enhancement efficiency also exhibits a monotonous increase from 1 to 5. Here, the enhancement efficiency is defined by the function $\eta = I_{Tsu+Con}/(I_{Tsu} + I_{Con})$, where $I_{Tsu}$, $I_{Con}$ and $I_{Tsu+Con}$ represent the green up-conversion luminescence intensities excited by the 800 nm Tsunami laser field, 980 nm Connet laser field and their combined laser field, respectively. However, when the 800 nm Tsunami laser intensity is fixed at 320 W $cm^{-2}$, the green up-conversion luminescence intensity also increases with the increase in the 980 nm Connet laser intensity, but the enhancement efficiency first increases and then decreases, and the maximal enhancement efficiency is about 5 with the 980 nm Connet laser intensity of 18 W $cm^{-2}$. Obviously, properly designing the 980 nm Connet laser intensity is necessary to maximally obtain the enhancement efficiency of the green up-conversion luminescence.

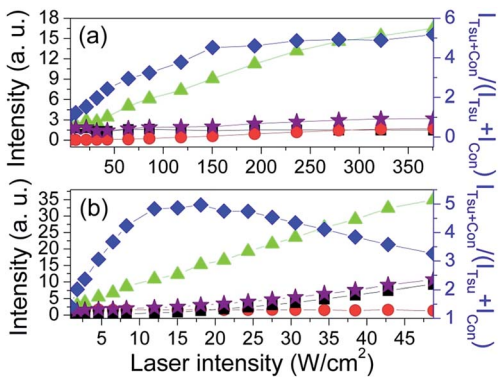


Fig. 3 Left coordinate: The green up-conversion luminescence intensity by varying the 800 nm Tsunami laser intensity while keeping the 980 nm Connet laser intensity at 20 W $cm^{-2}$ (a) and by varying the 980 nm Connet laser intensity while keeping the 800 nm Tsunami laser intensity at 320 W $cm^{-2}$ (b). Here, the red circles, black squares and green triangles represent the luminescence intensities excited by the 800 nm Tsunami laser field, 980 nm Connet laser field and their combined laser field, respectively. The purple stars are used to show the sum of the luminescence intensities excited by the two individual laser fields. Right coordinate: The enhancement efficiency of the green up-conversion luminescence intensity induced by the combined laser field with respect to the sum of that induced by the two individual laser fields $I_{Tsu+Con}/(I_{Tsu} + I_{Con})$ (blue rhombuses).

To better understand the green up-conversion luminescence enhancement mechanism in the $Er^{3+}/Yb^{3+}$-codoped glass sample by the two-color laser field excitation, we present the energy level diagrams of $Er^{3+}$ and $Yb^{3+}$ ions and the possible excitation processes of the green and red up-conversion luminescence, as shown in Fig. 4. Because the $Er^{3+}/Yb^{3+}$-codoped system is an activator/sensitizer structure, when the $Er^{3+}/Yb^{3+}$-codoped glass sample is excited by the 980 nm Connet laser field, the population in the ground state $^2F_{7/2}$ of $Yb^{3+}$ ions can be pumped to the excited state $^2F_{5/2}$ by the single photon absorption, which then returns to the ground state $^2F_{7/2}$ by the energy transfer to nearby $Er^{3+}$ ions. Due to the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions, the population in the ground state $^4I_{15/2}$ of $Er^{3+}$ ions can be pumped to the excited state $^4I_{11/2}$ by the single photon absorption, and then further pumped to the two higher excited states $^4F_{7/2}$ and $^4F_{9/2}$ by the two excited state absorptions $^4I_{11/2} \rightarrow {}^4F_{7/2}$ and $^4I_{13/2} \rightarrow {}^4F_{9/2}$; here, the population in the excited state $^4I_{13/2}$ results from the spontaneous decay of the excited state $^4I_{11/2}$. Because of the large absorption cross section of $Yb^{3+}$ ions and the high efficiency energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions, the luminescence efficiency of $Er^{3+}$ ions is usually higher. Here, the whole excitation process is called pathway P1. For the case that the $Er^{3+}/Yb^{3+}$-codoped glass sample is excited by the 800 nm Tsunami laser field, the population in the ground state $^4I_{15/2}$ of $Er^{3+}$ ions can be pumped to the excited state $^4I_{9/2}$ by the single photon absorption, and then further pumped to the three higher excited states $^2H_{9/2}$, $^4F_{3/2}$ and $^2H_{11/2}$ by the three excited state absorptions $^4I_{9/2} \rightarrow {}^2H_{9/2}$, $^4I_{11/2} \rightarrow {}^4F_{3/2}$ and $^4I_{13/2} \rightarrow {}^2H_{11/2}$, here the population in the two excited states $^4I_{11/2}$ and $^4I_{13/2}$ comes from the relaxation process of the excited state $^4I_{9/2}$. Similarly, the whole excitation process is called pathway P2. However, when both the 800 nm Tsunami and 980 nm Connet laser fields are used to excite the $Er^{3+}/Yb^{3+}$-codoped glass sample, in addition to the two individual excitation processes P1 and P2, there are also

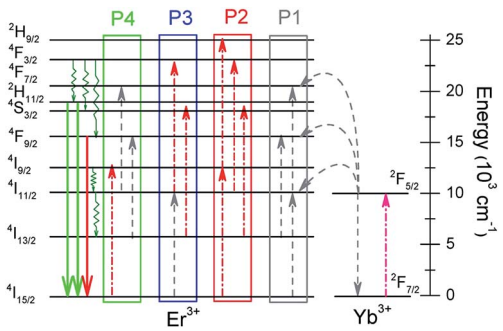


Fig. 4 The energy level diagrams of $Er^{3+}$ and $Yb^{3+}$ ions and the possible up-conversion excitation processes (P1–P4) of the green and red up-conversion luminescence.

two cooperative up-conversion excitation processes. The population in the ground state $^4I_{15/2}$ of $Er^{3+}$ ions is pumped to the excited state $^4I_{11/2}$ (or $^4I_{9/2}$) *via* the single-photon absorption by the 980 nm Connet (or 800 nm Tsunami) laser excitation, and then further pumped to the two excited states $^4F_{3/2}$ and $^2H_{11/2}$ (or $^4F_{7/2}$ and $^4F_{9/2}$) *via* the excited state absorption by the 800 nm Tsunami (or 980 nm Connet) laser excitation. The two cooperative up-conversion excitation processes are called pathways P3 and P4, respectively. In addition, the energy transfer up-conversion will also occur by the 800 nm Tsunami (or 980 nm Connet) laser field excitation,[35] but it will not affect the up-conversion luminescence enhancement efficiency, and thus here the excitation process is not considered.

One can see from Fig. 4 that the two excitation pathways P3 and P4 are both the possible reason for the green up-conversion luminescence enhancement of the $Er^{3+}/Yb^{3+}$-codoped glass sample by the two-color laser field excitation, and it is necessary to make sure which one is dominant. For the pathway P3, the population in the ground state $^4I_{15/2}$ is finally promoted to the excited states $^4F_{3/2}$ and $^2H_{11/2}$, and the population in the excited state $^4F_{3/2}$ can spontaneously decay to the three lower excited states $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$, which has the same effect on the green and red up-conversion luminescence, while the population in the excited state $^2H_{11/2}$ will mainly affect the green up-conversion luminescence. Similarly, for the pathway P4, the population in the ground state $^4I_{15/2}$ is finally pumped to the two excited states $^4F_{7/2}$ and $^4F_{9/2}$, and the population in the excited state $^4F_{7/2}$ will also relax to the three lower excited states $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$, and thus its effect on the green and red up-conversion luminescence is also the same, but the population in the excited state $^4F_{9/2}$ only contributes to the red up-conversion luminescence. Because our experimental results in Fig. 2(b) show that the green up-conversion luminescence can be greatly enhanced by the two-color laser field excitation while the red up-conversion luminescence is almost not affected; the dominant process for the green up-conversion luminescence enhancement should be attributed to the cooperative up-conversion excitation process P3, which contains the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions by the 980 nm laser field excitation and then the excited state absorption by the 800 nm laser field excitation.

To more clearly illustrate that the green up-conversion luminescence enhancement of the $Er^{3+}/Yb^{3+}$-codoped glass sample is due to the cooperative up-conversion excitation process P3, we study the green up-conversion luminescence intensity and its enhancement efficiency by varying the Tsunami laser wavelength, and the experimental results are shown in Fig. 5. Here, the tunable Tsunami laser intensity is fixed at 20 W $cm^{-2}$ and the 980 nm Connet laser intensity is kept at 320 W $cm^{-2}$. When the $Er^{3+}/Yb^{3+}$-codoped glass sample is only excited by the tunable Tsunami laser field, only one enhanced peak around the laser wavelength of 797 nm is observed with the laser wavelength scanning from 760 to 855 nm. However, when the 980 nm Connet laser field is added, another enhanced peak around the laser wavelength of 850 nm is obtained. Obviously, the 850 nm Tsunami laser field cannot induce the green up-conversion luminescence generation, but

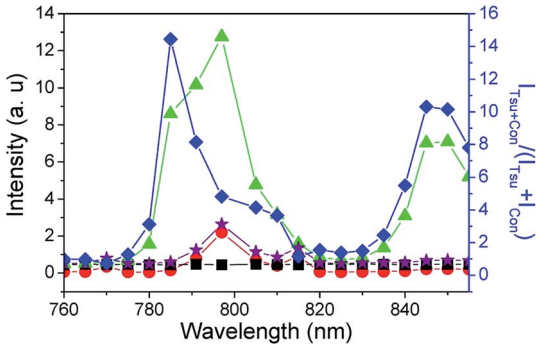


Fig. 5 The green up-conversion luminescence intensity by varying the tunable Tsunami laser wavelength (left coordinate), together with the enhancement efficiency of the luminescence intensity $I_{Tsu+Con}/(I_{Tsu} + I_{Con})$ (right coordinate). All the symbols are labeled the same as those shown in Fig. 3. Here, the tunable Tsunami and 980 nm Connet laser intensities are kept at 320 and 20 W $cm^{-2}$, respectively.

the two-color laser field by combining with the 850 nm Tsunami and 980 nm Connet laser fields can produce the green up-conversion luminescence enhancement. The 850 nm laser wavelength is corresponding to the state transition frequency from the excited state $^4I_{13/2}$ to $^4S_{3/2}$, and thus the green up-conversion luminescence enhancement should result from the cooperative up-conversion excitation process P3 *via* the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions by the 980 nm Connet laser field excitation and then *via* the excited state absorption $^4I_{13/2} \rightarrow {}^4S_{3/2}$ by the 850 nm Tsunami laser field excitation. Because no state absorption from the ground state $^4I_{15/2}$ can occur by the 850 nm Tsunami laser field excitation, the cooperative up-conversion excitation process P4 can be excluded.

On the basis of the energy level diagram of the $Er^{3+}$ ion in Fig. 4, the state absorption from the ground state $^4I_{15/2}$ to the excited state $^4I_{11/2}$ can also occur by the 980 nm Connet laser field excitation, and will also contribute to the green up-conversion luminescence enhancement. To show that the luminescence enhancement mainly comes from the contribution of the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions, we perform the same experiment in $Er^{3+}$-doped glass sample, which is prepared by the same method as the $Er^{3+}/Yb^{3+}$-codoped glass sample mentioned above, and the experimental result is shown in Fig. 6. Here, the experimental condition is the same as that in Fig. 2(b). One can see that the green up-conversion luminescence enhancement efficiency in an $Er^{3+}$-doped glass sample is only about 1.4, which is much smaller than that in the $Er^{3+}/Yb^{3+}$-codoped glass sample. The absorption cross-section of the $Yb^{3+}$ ion for the 980 nm Connet laser field excitation is much larger than that of the $Er^{3+}$ ion, and thus the population in the ground state $^4I_{15/2}$ of the $Er^{3+}$ ion is easy to be pumped to the excited state $^4I_{11/2}$ due to the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions, and the excitation efficiency is much higher than that of direct 980 nm laser field excitation. Thus, the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions in our experiment plays a decisive role in the green up-conversion luminescence enhancement by the two-color laser field excitation with the laser wavelengths of 800 (or 850) and 980 nm.

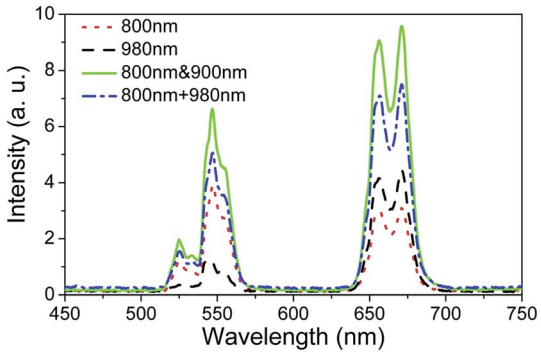


Fig. 6 The up-conversion luminescence spectra of an $Er^{3+}$-doped glass sample excited by the 800 nm Tsunami laser field (red dotted line), 980 nm Connet laser field (black dashed line) and their combined laser field (green solid line), together with the sum of the luminescence spectra excited by the two individual laser fields (blue dash-dotted line).

## 4. Conclusions

In summary, we have experimentally shown that the two-color laser field excitation with the laser wavelengths of 800 and 980 nm can provide a well-established tool to further improve the up-conversion luminescence efficiency of an $Er^{3+}/Yb^{3+}$-codoped glass sample. Our results showed that, compared with the sum of the up-conversion luminescence intensities induced by the two individual laser fields, the luminescence intensity from the combined two-color laser field can be greatly enhanced. Our analysis indicated that the luminescence enhancement is due to the involvement of other up-conversion excitation processes, and the cooperative up-conversion excitation process *via* the energy transfer from $Yb^{3+}$ to $Er^{3+}$ ions by the 980 nm laser field excitation and then the excited state absorption by the 800 nm laser field excitation as the main contribution. These results are very useful for designing the laser field to generate or enhance the up-conversion luminescence of lanthanide/$Yb^{3+}$-codoped luminescent materials, and can also be used as a research basis for future studies. Moreover, our scheme can also be further extended to the multi-color laser field excitation strategy. For example, the green up-conversion luminescence efficiency of the $Er^{3+}/Yb^{3+}$-codoped glass sample in our experiment can be further improved by the three-color laser field excitation with the laser wavelengths of 800, 850 and 980 nm. In addition, the up-conversion luminescence efficiencies by the dual-color (or multi-color) laser field excitation are usually different for different emission wavelengths, and thus it can also provide an efficient way to realize up-conversion luminescence tuning.

## Acknowledgements

This study was partly supported by the National Natural Science Foundation of China (No. 51132004 and No. 11474096) and Science and Technology Commission of Shanghai Municipality (No. 14JC1401500). We acknowledge the support of the NYU-ECNU Institute of Physics at NYU Shanghai.

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