# Upconversion mechanism for two-color emission in rare-earth-ion-doped ZrO<sub>2</sub> nanocrystals

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Two-color upconversion (UC) emissions with anomalous power dependence were observed in spectrally tailored rare-earth-ion-doped ZrO<sub>2</sub> nanocrystals. Single green and red UC radiation in the visible range was induced by 980 nm diode laser excitation in ZrO<sub>2</sub>: Er<sup>3+</sup> and ZrO<sub>2</sub>: Er<sup>3+</sup> +Yb<sup>3+</sup> nanocrystals, yielding quadratic and linear laser power dependences, respectively. The UC spectrum design is enabled by the saturation of the  ${}^{4}I_{13/2}(\text{Er})$  state through the efficient energy back-transfer process  ${}^{4}S_{3/2}(\text{Er}) + {}^{2}F_{7/2}(\text{Yb}) \rightarrow {}^{4}I_{13/2}(\text{Er}) + {}^{2}F_{5/2}(\text{Yb})$  induced by high Yb<sup>3+</sup>-ion concentration. The anomalous power dependence originates from the fact that the UC rate of the  ${}^{4}I_{11/2}(\text{Er})$  state at high Yb<sup>3+</sup>-ion concentrations is fundamentally much larger than its decay rate. These conclusions obtained are confirmed by theoretical investigations based on steady-state rate equations.

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## I. INTRODUCTION

Inorganic nanocrystals doped with rare-earth ions are of particular interest to be used as biological fluorescent labels due to their superior photostability, straightforward excitation, and background-free detection.<sup>1-6</sup> As compared with commonly used fluorescent labels, these upconversion (UC) labels circumvent problems such as photobleaching, induced by photochemical reactions in organic dyes, and high background, induced by ultraviolet excitation in quantum dots (QDs).<sup>4–6</sup> Additionally, low-cost, continuous-wave (cw), near-infrared (NIR) diode lasers, emitting radiation transparent for biomolecules, can be used to efficiently generate visible light, clearly contrasted with the traditional multiphoton labels, which require expensive mode-locked NIR lasers to generate visible light at low efficiency.<sup>1-6</sup> These superior characteristics distinguish UC labels from commonly used one- and multiphoton fluorescent labels and open up a new interesting research field in biological areas.

In our recent research, single green and red UC spectra in the visible range were designed for multicolor imaging applications by use of  $ZrO_2$ :  $Er^{3+}$  and  $ZrO_2$ :  $Er^{3+} + Yb^{3+}$  nanocrystals, respectively.<sup>6</sup> Single band emission refers to the fact that the designed main band is much stronger than the other impurity bands in the visible range.<sup>6</sup> The single band emissions of these materials distinguish them clearly from conventional UC labels, where several bands with substantial contributions are emitted simultaneously. Their characteristic spectra inherently avoid spectral cross talk and allow application in optical differentiation, e.g., bio-optical encoding, cell color imaging, and simultaneous tracking of multiple molecular targets.<sup>6-8</sup> It should be noted that weak UC emissions in the infrared (IR) range, e.g.,  ${}^{4}S_{3/2} \rightarrow {}^{4}I_{13/2}$ , are also present in the UC labels designed. However, their influence on biological applications can be easily suppressed by choosing a suitable sensitive detector-usually a non-IR sensitive photomultiplier tube. In this paper, we discuss the physical mechanisms to generate the two single color UC spectra, which is of significance for nanoscale science and design.

The UC spectra producing mechanisms in Er<sup>3+</sup>-ion-doped oxide nanomaterials have been widely discussed for hosts

such as  $Y_2O_3$ ,  $^{9-12}$  ZrO<sub>2</sub>,  $^{13-15}$  and Gd<sub>2</sub>O<sub>3</sub> nanocrystals.  $^{16,17}$ The similar Yb<sup>3+</sup>-ion dependence of the UC spectra in Yb<sup>3+</sup>-Er<sup>3+</sup>-ion-doped hosts under cw excitation of 980 nm may indicate a similar UC spectral tailoring mechanism.<sup>9-17</sup> However, different explanations in the literature are bestowed to the green and the red UC spectral tailorings, i.e., the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}(\text{Er})$  and the  ${}^{4}F_{9/2}(\text{Er})$  states are highly populated at low and high Yb<sup>3+</sup>-ion concentrations, respectively. This phenomenon has, for example, been ascribed to (a) the high Yb3+-ion-enhanced cross relaxation (CR) process and (c) the efficient energy back-transfer (EBT) process  ${}^{4}F_{7/2}(\text{Er}) + {}^{2}F_{7/2}(\text{Yb}) \rightarrow {}^{4}I_{11/2}(\text{Er}) + {}^{2}F_{5/2}(\text{Yb})$ , as well as the ET process  ${}^{4}I_{13/2}(\text{Er}) + {}^{2}F_{5/2}(\text{Yb}) \rightarrow {}^{4}F_{9/2}(\text{Er}) + {}^{2}F_{7/2}(\text{Yb}).^{16}$ However, none of the previous references can give a clear and detailed picture on the dynamic behavior of energy transitions induced by the high Yb3+-ion concentrations, e.g., why the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}(\text{Er})$  state can be completely depopulated and how the  ${}^{4}I_{13/2}(\text{Er})$  state is being highly populated. Although a small number of energy levels are involved to produce the visible UC emission, the UC mechanism is more complex than the simple experimental emission profiles seem to suggest.<sup>18</sup> Due to its key role for the emission characteristics, the UC pathway has significant influence on spectral design in nanotechnology and needs to be well understood. In this paper, high-Yb<sup>3+</sup>-ion-induced spectral tailoring and power dependence behaviors for two single color UC radiations under diode laser excitation of 980 nm are discussed in detail for their occurrence based on spectroscopic data and theoretical calculations. The conclusions obtained here may also apply to other Er<sup>3+</sup>-Yb<sup>3+</sup>-doped oxide nanocrystals.

## **II. EXPERIMENTAL METHODS**

 $ZrO_2$  powders doped with 1 mol %  $Er^{3+}$  and 0, 1, 2, 5, and 10 mol %  $Yb^{3+}$  ions were synthesized according to a



FIG. 1. (Color online) Measured XRD spectra of  $ZrO_2$  powders (a) doped with 1 mol %  $Er^{3+}$  and contrasted to the standard pattern of Ref. 27 and (b) doped with 1 mol %  $Er^{3+}$  and 10 mol %  $Yb^{3+}$ with the standard pattern of Ref. 28.

procedure described in detail in Ref. 6. The synthesis procedure is outlined here as follows:  $ZrO(NO_3)_2 \cdot 2H_2O$ ,  $Er(NO_3)_3 \cdot 6H_2O$ , and  $Yb(NO_3)_3 \cdot 5H_2O$  with corresponding molar ratio were first dissolved in de-ionized water to form a transparent solution, into which citric acid as a chelate and ammonium hydroxide as a *p*H adjuster were subsequently added. The solution was then dried to form a black bulk which was further calcined in air to generate the rare-earthion-doped  $ZrO_2$  nanocrystals. The structure of the prepared powders was identified by x-ray diffraction (XRD) using a Rigaku D/max- $\gamma$ B diffractometer. The  $2\theta$  angle of the XRD spectra was recorded from  $20^\circ$  to  $70^\circ$  at a scanning rate of  $5^\circ$ /min. The average crystallite sizes of the nanocrystals were calculated according to the following Scherrer's equation:

$$D = K\lambda/\beta\cos\theta,$$
 (1)

where K=0.89, D represents the crystallite size (in nanometers),  $\lambda$  is the wavelength of the Cu  $K\alpha$  radiation,  $\beta$  is the corrected half-width of the diffraction peak, and  $\theta$  is the Bragg's angle of the diffraction peak. Further, the powders were pressed to smooth and flat disks and irradiated by a focused 980 nm diode laser with a maximum power and power density of about 200 mW and 25 W/cm<sup>2</sup>, respectively. Thereby, room-temperature UC fluorescence was collected by a lens-coupled monochromator of 3 nm spectral resolution attached to a photomultiplier tube.

#### **III. RESULTS AND DISCUSSION**

## A. Crystal structure

Figure 1 displays the powder XRD patterns of the  $ZrO_2$  nanocrystals doped (a) with 1 mol %  $Er^{3+}$  and (b) with 1 mol %  $Er^{3+}$  and 10 mol %  $Yb^{3+}$ . Figure 1(a) shows that the crystal structure is tetragonal, corresponding well to the standard powder diffraction pattern of Ref. 27 referenced below. Interestingly, only cubic phase (Ref. 28) is observed in Fig. 1(b) when 10 mol % of  $Yb^{3+}$  ions are further introduced. The lattice parameters for Fig. 1(b) are calculated to be  $0.5134\pm0.0002$  nm, which is slightly larger than 0.5128 nm of Ref. 28, attributed to the larger size of the  $Yb^{3+}$  (0.1042 nm) and  $Er^{3+}$  (0.1062 nm) ions substituting the  $Zr^{4+}$ 



FIG. 2. (Color online) Fluorescence spectra of  $ZrO_2$  nanocrystals (a) doped with 1 mol %  $Er^{3+}$  and (b) doped with 1 mol %  $Er^{3+}$  and 10 mol %  $Yb^{3+}$  under 980 nm wavelength laser excitation. The two spectra were normalized to the highest values.

(0.089 nm) ion in the crystal lattice with charge compensation by oxygen vacancy.<sup>19,20</sup> Furthermore, the diffraction peaks are broadened as compared to the peaks in Fig. 1(a). The average particle diameter, according to the aforementioned Scherrer's equation, was calculated to be about 29 and 18 nm for Figs. 1(a) and 1(b), respectively. This demonstrates the significance of the Yb<sup>3+</sup> ions on the particle size, which has to be considered for biological application, since nearly uniform nanocrystal size is a prerequisite for displaying similar dynamic behavior. The fabrication of sizecontrolled and monodisperse ZrO<sub>2</sub> nanocrystals via a special chemical route is the focus of our forthcoming work in order to achieve water-soluble and biocompatible UC labels by employing a core-shell structure.

## **B.** Upconversion emission

Figure 2 shows the single green UC fluorescent band at 525/545 nm [Fig. 2(a)] and the single red UC fluorescent band at 655 nm [Fig. 2(b)] in the visible range, achieved in ZrO<sub>2</sub>:Er<sup>3+</sup> 1 mol % and ZrO<sub>2</sub>:Er<sup>3+</sup> 1 mol %, Yb<sup>3+</sup> 10 mol % nanocrystals, respectively. The red and the green fluorescent radiations correspond to the intra 4f-4f electronic transitions  ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$  and  ${}^{2}H_{11/2}/{}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$  of the Er<sup>3+</sup> ions, respectively. Note that the two UC labels have optically resolvable pure color radiations under the same wavelength excitation of 980 nm and bandwidths of about 60 nm which are comparable to those of QDs. Such characteristics can allow them to be used for a variety of biological multicolor applications such as cellular multicolor imaging, simultaneous tracking of multiple targets, and relative quantification analysis of several label concentrations. Comparison of Fig. 2(b) with Fig. 2(a) indicates that complete depopulation of the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}(\text{Er})$  state and enhanced population of the  ${}^{4}F_{9/2}(\text{Er})$  state are simultaneously induced by the high Yb<sup>3+</sup>-ion concentration, since only pure red emission is emitted in Fig. 2(b), which is about 35 times more intense than the pure green one in Fig. 2(a). Further, the pump power dependence of the two-color UC fluorescent radiations was investigated. It is known that for unsaturated UC processes, the number of photons which are required to populate the upper emitting state can be obtained by the following relation:21



FIG. 3. (Color online) Pump power dependence of the single green fluorescent band emission in  $ZrO_2:Er^{3+}$  1 mol % nanocrystals and of the single red fluorescent band emission in  $ZrO_2:Er^{3+}$  1 mol %, Yb<sup>3+</sup> 10 mol % nanocrystals in a logarithmic diagram.

$$I_f \propto P^n$$
, (2)

where  $I_f$  is the fluorescent intensity, P is the pump laser power, and n is the number of the laser photons required. As shown in Fig. 3, the n values for the green and the red emissions are 1.83 and 1.22, which means that two- and onephoton processes are involved to populate the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}$ and the  ${}^{4}F_{9/2}$  states, respectively. This seems rather confusing, because at least a two-photon process is expected for both of them following the energy conservation law (consult Fig. 4).

#### C. Mechanisms of upconversion emission

Figure 4 shows the energy level diagrams of the Er<sup>3+</sup> and the Yb<sup>3+</sup> ions, as well as the proposed UC processes under laser excitation of 980 nm.<sup>22</sup> The laser photons resonantly match the level space  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$  of the Er<sup>3+</sup> ion and  ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$  of the Yb<sup>3+</sup> ion. As for the green emission in ZrO<sub>2</sub> nanocrystals doped with 1 mol % Er<sup>3+</sup> ions [Fig. 2(a)], the Er<sup>3+</sup> ion absorbs one laser photon and jump from the ground state to the long-lived  ${}^{4}I_{11/2}$  state. Then, excited state absorption or ETO occurs and populates the  ${}^{4}F_{7/2}$  state. Subsequently, the Er<sup>3+</sup> ions at this state are relaxed rapidly to the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}$  state by multiphonon processes, from which the



FIG. 4. (Color online) Energy level diagram of  $Er^{3+}$  and  $Yb^{3+}$  ions as well as the proposed UC mechanism in  $ZrO_2$  nanocrystals doped with 1 mol %  $Er^{3+}$  ions (left) and codoped with 1 mol %  $Er^{3+}$  and 10 mol %  $Yb^{3+}$  ions (right) under laser excitation of 980 nm. For symbols in the figure, see reference in Sec. III D.



FIG. 5. (Color online) Pump power dependence of the green emission of  $ZrO_2$  nanocrystals doped with constant 1 mol %  $Er^{3+}$  ion and with different Yb<sup>3+</sup>-ion concentrations in a logarithmic diagram ( $\blacksquare$ , 1 mol %;  $\bullet$ , 2 mol %; and  $\blacktriangle$ , 5 mol %).

single green emission arises. This is clearly a two-step and two-photon process by noting that the population in the  ${}^{4}I_{11/2}$ state is proportional to the power of the laser. Here, as pictured in Fig. 2(a), red UC emission from the  ${}^{4}F_{9/2}$  state can hardly arise, since the  ${}^{4}F_{9/2}$  state has a large energy gap of about 3059 cm<sup>-1</sup> below the  ${}^{4}S_{3/2}$  state, more than six times the phonon energy of the  $ZrO_2$  lattice (470 cm<sup>-1</sup>).<sup>14</sup> There is always some contamination with high phonon energy (OH of  $3400 \text{ cm}^{-1}$  and CO of  $1500 \text{ cm}^{-1}$ ) on the surface of UC nanocrystals,<sup>11,16</sup> which can induce efficient nonradiative processes. However, from Fig. 2(a), we can conclude that nonradiative effects induced by surface contamination are negligible, since the  ${}^{4}F_{9/2}$  state is almost not populated by the above  ${}^{4}S_{3/2}$  state. In addition, the nonradiative contribution to the population of the  ${}^{4}I_{13/2}(\text{Er})$  state from the above excited  ${}^{4}I_{11/2}(\text{Er})$  state can also be neglected, since almost no red emission exists in Fig. 2(a), which agrees with the fact that the energy gap is about 3326  $\text{cm}^{-1}$  of more than seven times the phonon energy of the  $ZrO_2$  lattice.

As pictured in Figs. 2 and 3, when  $Yb^{3+}$  ions of 10 mol % are further introduced, we note that, firstly, the UC spectrum is changed from single green to enhanced single red fluorescent band emission and, secondly, the power dependence of the UC emission is changed from quadratic to linear. These two facts indicate the importance of the  $Yb^{3+}$  ions in the UC mechanism to generate the spectrum of Fig. 2(b). To address these changed behaviors and investigate the role of the  $Yb^{3+}$  ions in the UC process, we measured the power dependence of the green and the red UC emissions as well as the UC spectra as a function of increasing  $Yb^{3+}$ -ion concentrations, as shown in Figs. 5–7, respectively.

Figure 5 shows that the *n* values are about 2 for both the 1 and 2 mol % Yb<sup>3+</sup>-ion concentrations, where *n* is the number of laser photons required to produce the green UC emission. It indicates that the green emission is a two-photon process for these two Yb<sup>3+</sup>-ion concentrations. This result is consistent with the well-known fact that in Yb<sup>3+</sup>-Er<sup>3+</sup> codoped materials (at low Yb<sup>3+</sup>-ion concentration), the  ${}^{4}F_{7/2}$  state is populated by two ET steps (ET1 and ET3) from the Yb<sup>3+</sup> to the Er<sup>3+</sup> ion, as illustrated in Fig. 4. Moreover, the mechanism discussed here differs from that of the aforementioned ZrO<sub>2</sub>:Er<sup>3+</sup> 1 mol % nanocrystals, because the Yb<sup>3+</sup>



FIG. 6. (Color online) Pump power dependence of the red emission of  $\text{ZrO}_2$  nanocrystals doped with constant 1 mol %  $\text{Er}^{3+}$  ion and with different Yb<sup>3+</sup>-ion concentrations in a logarithmic diagram ( $\blacksquare$ , 1 mol %;  $\blacksquare$ , 2 mol %;  $\blacktriangle$ , 5 mol %; and  $\blacktriangledown$ , 10 mol %).

ion has a much larger absorption cross section than that of the Er<sup>3+</sup> ion under laser excitation of 980 nm. In addition, it is noted that n=2.37 is obtained for the Yb<sup>3+</sup>-ion concentration of 5 mol %. This value deviates significantly from *n* =2 and may imply a different UC mechanism to produce green fluorescence. At high Yb3+-ion concentration, the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}(\text{Er})$  state can be populated via a three-photon process by nonradiative relaxation from the higher  ${}^{4}G_{11/2}(\text{Er})$ state, which is populated via a one-photon process by ET from the Yb<sup>3+</sup> to the Er<sup>3+</sup> ion in the  ${}^{4}F_{9/2}$  state (ET4, see Fig. 4).<sup>12,23</sup> By noting the fact that n=1.33 is obtained for populating the  ${}^{4}F_{9/2}(\text{Er})$  state at Yb<sup>3+</sup>-ion concentration of 5 mol % (Fig. 6), an additional one-photon process will lead to n=2.33 for populating the  ${}^{4}G_{11/2}(\text{Er})$  state, which agrees well with the observed value of n=2.37. Additionally, the n value for a Yb<sup>3+</sup>-ion concentration of 10 mol % is not given in Fig. 5 due to complete quenching of the UC green emission. The theoretical reasons for obtaining different n values of UC emissions at different Yb<sup>3+</sup>-ion concentrations will be discussed in detail in the following section.

For the red emission in Fig. 6, the *n* values are 1.74 and 1.55 for Yb<sup>3+</sup>-ion concentrations of 1 and 2 mol %, respectively, which indicate a two-photon process for producing the red band. Unexpectedly, the *n* values decrease to 1.33 and 1.22 for Yb<sup>3+</sup>-ion concentrations of 5 and 10 mol %, respec-



FIG. 7. (Color online) UC spectra of various  $ZrO_2$ :  $Er^{3+}$  (1 mol %), Yb<sup>3+</sup> (1, 2, 5, and 10 mol %) nanocrystals under 980 nm excitation. All spectra were normalized to the highest values.

tively, as the Yb<sup>3+</sup>-ion concentration increases. It seems that at high Yb<sup>3+</sup>-ion concentrations, only a "one-photon" process is needed to excite the electrons to the  ${}^{4}F_{9/2}(\text{Er})$  state where red fluorescence arises.

Combining the discussions for Figs. 2, 5, and 6, it shows that the key question is to explain high-Yb<sup>3+</sup>-induced onephoton phenomenon for highly populating the  ${}^{4}F_{9/2}(\text{Er})$ state. Figure 7 shows that the relative intensity of the red UC emission to the green UC emission increases greatly as the Yb<sup>3+</sup>-ion concentration increases. This indicates the key role of Yb<sup>3+</sup> ions in tuning the populations of Er<sup>3+</sup> ions between the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}(\text{Er})$  state and the  ${}^{4}F_{9/2}(\text{Er})$  state. As can be seen, the green emission can be completely quenched at a 10 mol % Yb3+-ion concentration, which indicates the zero population of the  ${}^{2}H_{11/2}/{}^{4}S_{3/2}(\text{Er})$  state induced by the high Yb<sup>3+</sup>-ion concentration. It should further be noted that the  ${}^{4}F_{9/2}(\text{Er})$  state is populated by excitation via ET2 (see Fig. 4) of the long-lived  ${}^{4}I_{13/2}(\text{Er})$  state (lifetime of about 8 ms).<sup>24</sup> Considering the steady-state nature of the system, due to the cw excitation, the quenching of the UC green emission and the high population of the  ${}^{4}F_{9/2}(\text{Er})$  state must be induced by saturation of the  ${}^{4}I_{13/2}(\text{Er})$  state, which can also explain the anomalous one-photon process for producing the red UC emission in Fig. 6. The aforementioned value of n=2.37 for the green emission in Fig. 5 can also be thoroughly explained by the saturation effect, which results in n = 1.33 for populating the  ${}^{4}F_{9/2}(\text{Er})$  state and n=2.33 for populating the  ${}^{4}G_{11/2}(\text{Er})$  state. For comparison, in the well documented Ref. 25, the anomalous power dependence of single-iondoped materials has been fundamentally attributed to the competition between the UC rate and the linear decay. However, the anomalous behavior here is induced by the Yb<sup>3+</sup> ions, and not by the laser intensity in the single-ion-doped case. In practice, Yb<sup>3+</sup> ions can play the role of laser intensity, since the increased ratio of Yb<sup>3+</sup> ions per Er<sup>3+</sup> ion and the shorter distance between Er<sup>3+</sup> and Yb<sup>3+</sup> ions can strongly influence the UC rate. Therefore, the anomalous power dependence and the saturation effect of the ion-codoped materials need more careful and fundamental investigations.

Let us consider two mechanisms shown in Fig. 4 that could possibly induce saturation of the  ${}^{4}I_{13/2}(\text{Er})$  state: one is the EBT process  ${}^{4}S_{3/2}(\text{Er}) + {}^{2}F_{7/2}(\text{Yb}) \rightarrow {}^{4}I_{13/2}(\text{Er}) + {}^{2}F_{5/2}(\text{Yb})$ ,<sup>12</sup> and the other is the enhanced CR process of the  $\text{Er}^{3+}$  ions  ${}^{2}H_{11/2} + {}^{4}I_{15/2} \rightarrow {}^{4}I_{9/2} + {}^{4}I_{13/2}$ .<sup>9,15</sup> The energy mismatch in the EBT process is about 320 cm<sup>-1</sup> and can be easily dissipated by one phonon of the ZrO<sub>2</sub> lattice  $(470 \text{ cm}^{-1})$ . Thus, the EBT process is inherently efficient and becomes more prominent for higher Yb<sup>3+</sup>-ion concentration due to reduced average distance between the Yb<sup>3+</sup> and the  $Er^{3+}$  ions and the increased ratio of  $Yb^{3+}$  ions per  $Er^{3+}$  ion. We believe that the EBT process is dominating at high Yb<sup>3+</sup>-ion concentration, e.g., 10 mol %, due to the following: Firstly, the CR process cannot saturate the  ${}^{4}I_{13/2}(\text{Er})$  state, since an efficient CR process requires a large number of Er<sup>3+</sup> ions in the  ${}^{2}H_{11/2}$  and the ground state simultaneously, which contradicts saturation of the  ${}^{4}I_{13/2}(\text{Er})$  state. Secondly, the CR process cannot quench the green emission [see Fig. 2(b)], since an efficient CR process requires a large population in the  ${}^{2}H_{11/2}$  state, thereby resulting in an efficient green emission, which contradicts the experimental observations. We therefore conclude that saturation of the  ${}^{4}I_{13/2}(\text{Er})$  state arises from the efficient EBT process.

#### **D.** Theoretical description

To verify and make a theoretical interpretation of the power dependence behavior and the saturation behavior of the  ${}^{4}I_{13/2}(\text{Er})$  state, we utilized the following steady-state equations:

$$W_0 N_0 N_{\rm Yb1} - R_2 N_2 - W_2 N_2 N_{\rm Yb1} = 0, \qquad (3)$$

$$W_2 N_2 N_{\rm Yb1} - R_4 N_4 - W' N_4 N_{\rm Yb0} = 0, \qquad (4)$$

$$W'N_4N_{\rm Yb0} - W_1N_1N_{\rm Yb1} = 0, (5)$$

$$W_1 N_1 N_{\rm Yb1} - R_3 N_3 = 0, (6)$$

 $I\sigma N_{\rm Yb0}/h\nu + W'N_4N_{\rm Yb0}$ 

$$-(W_0N_0 + W_1N_1 + W_2N_2)N_{Yb1} - RN_{Yb1} = 0, \qquad (7)$$

where  $N_0$  ( $W_0$ ),  $N_1$  ( $W_1$ ,  $R_1$ ),  $N_2$  ( $W_2$ ,  $R_2$ ),  $N_3$  ( $W_3$ ,  $R_3$ ), and  $N_4$  ( $W_4$ ,  $R_4$ ) are the population densities (energy-transfer rates from excited Yb<sup>3+</sup> ions, radiation rates) of the <sup>4</sup> $I_{15/2}$ , <sup>4</sup> $I_{13/2}$ , <sup>4</sup> $I_{11/2}$ , <sup>4</sup> $F_{9/2}$ , and <sup>4</sup> $S_{3/2}$  states, respectively, of the Er<sup>3+</sup> ions;  $N_{Yb0}$  and  $N_{Yb1}$  are the population densities of the Yb<sup>3+</sup> ions in the ground and the excited states, respectively (see Fig. 4); W' is the energy-transfer rate back to the Yb<sup>3+</sup> ion; I is the laser intensity and  $\nu$  is the laser frequency; and  $\sigma$  denotes the absorption cross section of the Yb<sup>3+</sup> ion, while R is the radiation rate of the <sup>2</sup> $F_{5/2}$ (Yb) state.

In the following discussion, the radiation decay of the  ${}^{4}I_{13/2}$  state in Eq. (5) is omitted as compared to the UC rate from this state due to its longest lifetime of several milliseconds, which creates a good population reservoir for excited  $\mathrm{Er}^{3+}$  ions. Additionally, it is reasonable to neglect the contribution to the population of the  ${}^{2}F_{5/2}(\mathrm{Yb})$  state resulting from the EBT process in Eq. (7), when compared to that induced by the laser excitation. This is because that the Yb<sup>3+</sup>-ion density dominates and it has much larger absorption cross section than the  $\mathrm{Er}^{3+}$  ion, and the interaction between ions is much less than the laser-ion interaction. Thus, from Eq. (7), we obtain

$$N_{\rm Yb1} = \sigma N_{\rm Yb0} I / (R + W_0 N_0 + W_1 N_1 + W_2 N_2) h \nu \propto I.$$
 (8)

At lower Yb<sup>3+</sup>-ion concentrations, e.g.,  $1-2 \mod \%$ , the linear decay rate from the  ${}^{4}I_{11/2}(\text{Er})$  state,  $R_2N_2$ , should be larger than the UC rate, and thus, the UC rate  $W_2N_2N_{\text{Yb1}}$  in Eq. (3) can be neglected. From Eqs. (3)–(8), we get

$$N_4 = W_0 W_2 N_0 N_{\rm Yb1}^2 / R_2 (R_4 + W' N_{\rm Yb0}) \propto I^2, \qquad (9)$$

$$N_3 = W_0 W_2 W' N_0 N_{\rm Yb0} N_{\rm Yb1}^2 / R_3 R_2 (R_4 + W' N_{\rm Yb0}) \propto I^2.$$
(10)

These results agree well with the experiments, where the green and the red emissions were found to involve two-

photon processes. At higher Yb<sup>3+</sup>-ion concentration, e.g.,  $5-10 \mod \%$ , the UC rate  $W_2N_2N_{Yb1}$  dominates and the linear decay  $R_2N_2$  can be neglected in Eq. (3). In contrast, we have

$$N_4 = W_0 N_0 N_{\rm Yb1} / (R_4 + W' N_{\rm Yb0}) \propto I, \tag{11}$$

$$N_3 = W_0 W' N_0 N_{\rm Yb0} N_{\rm Yb1} / R_3 (R_4 + W' N_{\rm Yb0}) \propto I, \qquad (12)$$

$$N_1 = W_0 W' N_{\rm Yb0} N_0 / W_1 (R_4 + W' N_{\rm Yb0}).$$
(13)

Since the EBT process is the predominant mechanism for depopulating the  ${}^{4}S_{3/2}(\text{Er})$  state, Eqs. (11)–(13) simply yield

$$N_4 = W_0 N_0 N_{\rm Yb1} / W' N_{\rm Yb0} \approx 0, \qquad (14)$$

$$N_3 = W_0 N_0 N_{\rm Yb1} / R_3, \tag{15}$$

$$N_1 = W_0 N_0 / W_1 = N_0. \tag{16}$$

It should be noted that  $N_{Yb0}$  is much larger than  $N_{Yb1}$ , and thus  $N_4$  can be neglected as compared to  $N_3$ . It indicates that the green emission can be quenched and the red emission can be greatly enhanced when the EBT process is highly efficient. This agrees well with the observed experimental data. Equation (16) indicates the saturation effect of the  ${}^{4}I_{13/2}(\text{Er})$ state and demonstrates our proposed UC mechanism, since  $N_1$  is proportional to the population  $N_0$  in the ground state. Further,  $W_0$  and  $W_1$  are expected to be equal resulting in  $N_1 = N_0$  due to the following: The  ${}^4I_{13/2}(\text{Er})$  state is similar to the ground state, and ET1 and ET2 at room temperature are nearly resonant. Therefore,  $W_0$  and  $W_1$  can be evaluated by the Förster law which depends on the decay time of the sensitizer and the distance between the sensitizer and the activator.<sup>26</sup> These two factors are the same for both  $W_0$  and  $W_1$ , thus yielding almost the same magnitude. The anomalous power dependence of the red emission can now be explained more fundamentally and thoroughly by the fact that the UC rate at the  ${}^{4}I_{11/2}(\text{Er})$  state is larger than the linear decay rate induced by high Yb<sup>3+</sup>-ion concentrations. It can be noted that in Eq. (14), the *n* value is 1.0, which is in disagreement with the experimental data of n=2.3. This is due to the fact that the population from the upper state of  ${}^{2}H_{9/2}(\text{Er})$  is out of consideration in Eq. (4). Combining the zero population of the  ${}^{4}S_{3/2}(\text{Er})$  state in our result and the upper state depopulation for generating green UC emission, the experimental data can be easily verified.

## **IV. CONCLUSIONS**

In summary, to develop fluorescent labels, rare-earth-iondoped ZrO<sub>2</sub> nanocrystals were produced by a complex precursor method. Single green and red fluorescent band UC emissions in the visible range were achieved in ZrO<sub>2</sub>: Er<sup>3+</sup> 1 mol % and in ZrO<sub>2</sub>: Er<sup>3+</sup> 1 mol %, Yb<sup>3+</sup> 10 mol % nanocrystals, respectively. The UC spectra tailoring from single green emission to single red emission arises from the saturation of the  ${}^{4}I_{13/2}$ (Er) state, which is induced by the efficient EBT process  ${}^{4}S_{3/2}$ (Er) + ${}^{2}F_{7/2}$ (Yb)  $\rightarrow {}^{4}I_{13/2}$ (Er) + ${}^{2}F_{5/2}$ (Yb). The single green fluorescent band shows a quadratic laser power dependence, whereas the single red fluorescent band shows a nearly linear laser power dependence. This anomalous power dependence can be explained by the saturation of the  ${}^{4}I_{13/2}(\text{Er})$  state; however, more fundamentally, it can be ascribed to the fact that the UC rate is much larger than the linear decay rate of the  ${}^{4}I_{11/2}(\text{Er})$  state, which is induced by

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the high Yb<sup>3+</sup>-ion concentration of 10 mol %.

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