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Magnetic field enhanced upconversion luminescence and magnetic–optical hysteresis behaviors in NaYF$_4$: Yb, Ho nanoparticles†

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Upconversion, an anti-Stokes process converting two or more low energy photons into a high energy photon, has received much attention due to its wide applications ranging from photonics to medicine. As a nonlinear optical process, the efficiency of upconversion is inherently low, which strongly limits the applications of upconversion. Here we report the enhancement of upconversion luminescence in NaYF$_4$: Yb, Ho nanoparticles with a pulse magnetic field. The intensity of emissions from $^5S_2$, $^5F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2$, $^5F_4 \rightarrow {}^5I_7$ transitions has been increased 1.71, 1.93, 1.68 times respectively. The enhanced emission has been ascribed to the enhanced energy transfer from Yb^{3+} to Ho^{3+} with increasing magnetic field intensity. Besides, the magnetic–optical hysteresis behaviors of upconversion luminescence intensity have also been observed when the magnetic field was scanned from 0 T to 40 T. This is connected with the sluggish kinetics of spin re-orientation of the paramagnetic lanthanide ions in the pulse magnetic field. The magnetic field modulated upconversion luminescence demonstrated here might provide a new approach to enhance the upconversion efficiency.

Upconversion, a process converting two or more low energy photons into a high energy photon, has attracted much attention for its wide applications in solid-state lasers, optical data storage, bioimaging and so on.[1–4] Compared with the traditional

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materials, upconversion luminescence from lanthanide ions features sharp emission bandwidth, larger anti-Stokes shift and high chemical stability.[5–7] Especially, the upconversion luminescence from Yb^{3+}–Ho^{3+} ion pairs exhibits high efficiency due to the favourable energy transfer from Yb^{3+} to Ho^{3+} with the near infrared excitation. The strong near-infrared luminescence from Ho^{3+} by the transitions of $^5F_5 \rightarrow {}^5I_8$ and $^5F_4$, $^4S_2 \rightarrow {}^5I_7$ makes Yb^{3+}–Ho^{3+} doped nanoparticles highly competitive for different bioimaging applications.[8–11] On the other hand, the utilization of cross relaxation between Ho^{3+} and other lanthanide ions allows for the facile tuning of the emission bands and the universal process-inert encoding architecture.[12–14] In spite of the diverse applications, the upconversion efficiency for most lanthanide ions including Yb^{3+}–Ho^{3+} still suffers from the low efficiency.[15] There has been a constant need to search for an efficient approach to modulate the upconversion spectra and improve the upconversion efficiency.

Magnetic field modulated the luminescence from lanthanide ions has been reported in the last few years.[16–19] Much attention has been paid to the upconversion luminescence behaviors of Er^{3+} ion with the doping matrix of glass, phosphor and nanoparticles in the presence of magnetic field.[20–28] There is no report up to now concerning the upconversion luminescence from Ho^{3+} with the application of magnetic field. Besides, the investigation of magnetic samples in the range of 1–100 nm, where the quantum and classical effects coexists, has been developed in the last few days due to its physics significance.[29,30] Therefore, there might be some novel magnetic–optical interaction in the upconversion luminescence of Ho^{3+} induced by spin–phonon and spin–spin coupling at nanoscale with the application of magnetic field.

In this paper, we synthesized the Ho^{3+} doped hexagonal NaYF$_4$ nanoparticles and detected the upconversion luminescence modulated by magnetic field. The enhanced upconversion luminescence from the transitions of $^5S_2$, $^5F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2$, $^5F_4 \rightarrow {}^5I_7$ of Ho^{3+} has been observed for the first time, which is ascribed to the enhanced energy transfer from Yb^{3+} to Ho^{3+} with increasing the magnetic field intensity. The

splitting and broadening of emission bands induced by Zeeman effect have also been detected. Besides, the magnetic–optical hysteresis behaviors of upconversion luminescence intensity of Ho^{3+} have been discovered for the first time with changing the magnetic field intensity, which are interpreted in terms of the delay spin re-orientation of Ho^{3+} in the response to the pulse magnetic field. The magnetic field modulated upconversion luminescence may offer a new approach for the manipulation of the upconversion efficiency.

The hexagonal $NaYF_4$: 20% Yb, 1% Ho nanoparticles were synthesized by the co-precipitation method with the oleic acid (OA) and 1-octadecene (ODE) system.[5] The low-resolution transmission electron microscopy (TEM) image given in Fig. 1A shows the typical morphology and size of hexagonal $NaYF_4$ nanoparticles with the rod-like and narrow size distribution. The high-resolution TEM (HRTEM) image of a single

$NaYF_4$: 20% Yb, 1% Ho nanoparticle (Fig. 1B) reveals the single crystalline structure of the nanoparticle. A typical planar distance of 0.508 nm is found, which is corresponding to the d spacing for (100) lattice planes. The crystal structure was further characterized by the X-ray diffraction (XRD) analysis. The XRD patterns (Fig. 1C) of the product are all matched well with the calculated patterns for β-$NaYF_4$ (JCPDS no. 16-0334), indicating the high-purity phase of the prepared nanoparticles.

The luminescence spectrum of $NaYF_4$: 20% Yb, 1% Ho nanoparticles without magnetic field was recorded under the excitation at 975 nm and 90 K (Fig. 2A). Three emission bands around 540 nm, 650 nm, and 750 nm were observed, which are ascribed to the transitions of $^5S_2$, $^5F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2$, $^5F_4 \rightarrow {}^5I_7$ of Ho^{3+},[31] respectively. The energy level diagram (Fig. 2B) of the Yb^{3+}–Ho^{3+} ion pair illustrates the energy transfer pathways and the possible radiative transitions,[32] suggesting the two-photons upconversion process for $^5S_2$, $^5F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2$, $^5F_4 \rightarrow {}^5I_7$ transitions of Ho^{3+}.

Magnetic field tuned upconversion luminescence spectra of the powdered nanoparticles were measured by a home-built luminescence spectroscopy system equipped with a pulsed magnetic field (Fig. S1†) and 975 nm laser diode (200 mW) at 90 K. Fig. 3 and S2† show the luminescence spectra of $NaYF_4$: 20% Yb, 1% Ho nanoparticles from the transitions of $^5S_2$, $^5F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ and $^5S_2$, $^5F_4 \rightarrow {}^5I_7$ of Ho^{3+} at different magnetic field intensities. The steady splitting of the emission peaks and broadening of the emission bands from $^5S_2$, $^5F_4 \rightarrow {}^5I_8$ transition with increasing the magnetic field intensity were observed in Fig. 3A which can be explained by the Zeeman effect induced by magnetic field. The external magnetic field induced an external torque to the energy levels of lanthanide ions, causing an external energy to the energy levels and resulting in the energy level with the total angular moment J splitting into $2J + 1$ Zeeman sub-levels for the different g factor of the sub-levels.[16] The energy level splitting induced by magnetic field leads to the splitting of the emission peaks and the blue-shift of the emission bands in high energy region and the red-shift of the emission bands located at low energy region. However, the magnetic field modulated luminescence spectra of $NaYF_4$: 20%
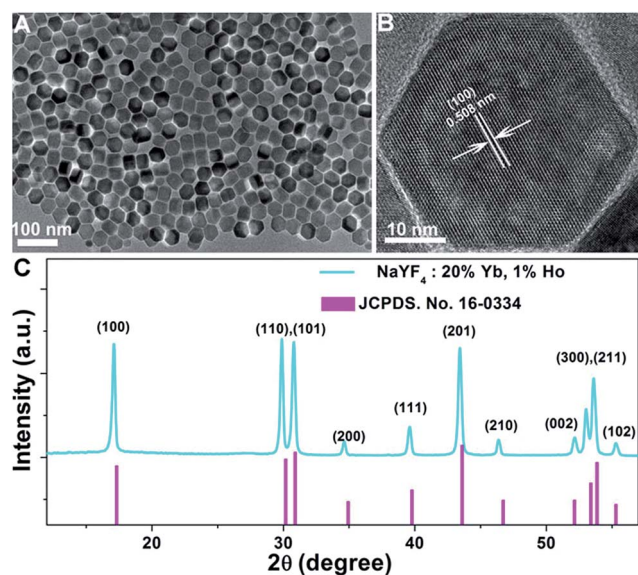

Fig. 1 (A) TEM image of $NaYF_4$: 20% Yb, 1% Ho nanoparticles, (B) HRTEM image of single $NaYF_4$: 20% Yb, 1% Ho nanoparticle, (C) XRD patterns of $NaYF_4$: 20% Yb, 1% Ho nanoparticles.
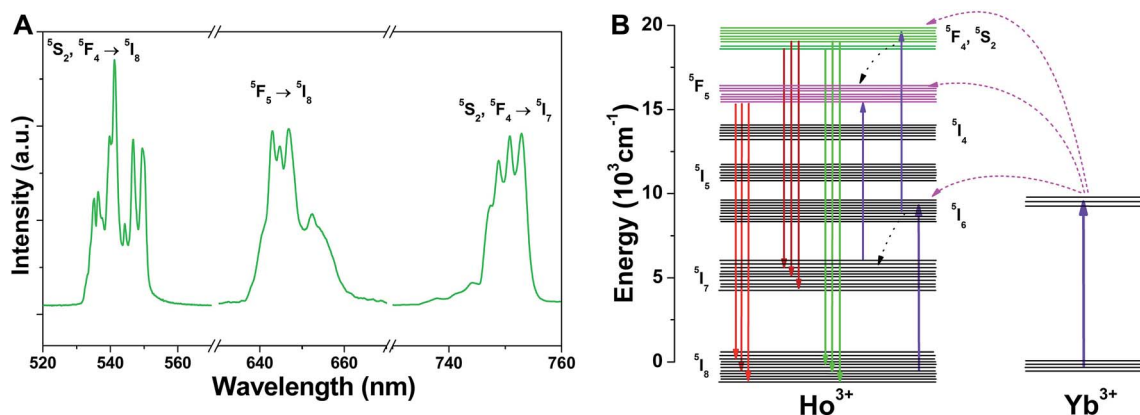

Fig. 2 (A) Luminescence spectrum of $NaYF_4$: 20% Yb, 1% Ho nanoparticles under the excitation at 975 nm without magnetic field at 90 K. (B) Schematic energy level diagram of the Yb^{3+}–Ho^{3+} ion pair. Energy transfer pathways and the possible radiative transitions are indicated.
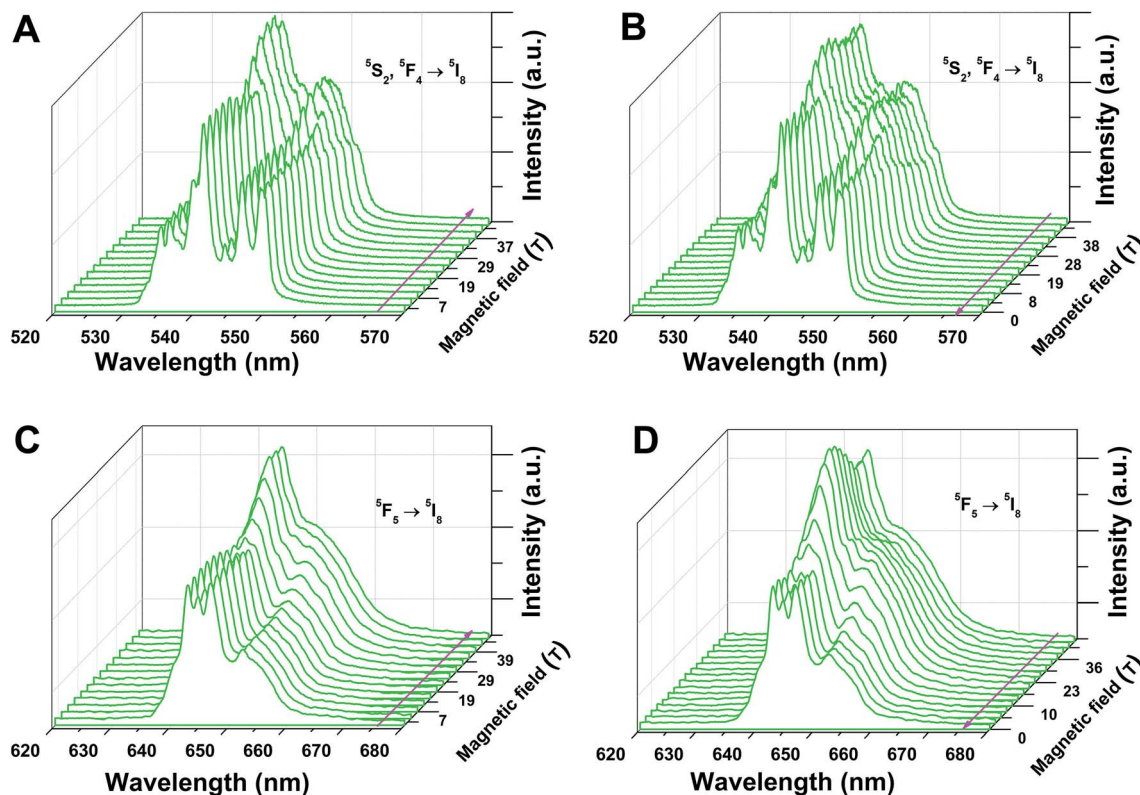
Fig. 3 (A and B) Luminescence spectra of NaYF$_4$: 20% Yb, 1% Ho nanoparticles from the transition of $^5S_2$, $^5F_4 \rightarrow {}^5I_8$ with increasing (A) and decreasing (B) magnetic field. (C and D) Luminescence spectra of NaYF$_4$: 20% Yb, 1% Ho nanoparticles from the transition of $^5F_5 \rightarrow {}^5I_8$ with increasing (C) and decreasing (D) magnetic field.

Yb, 1% Ho nanoparticles from $^5F_5 \rightarrow {}^5I_8$ transition of Ho^{3+} (Fig. 3C) reveal the merging of the emission peaks with increasing the magnetic field intensity. The merging of the emission peaks for the $^5F_5 \rightarrow {}^5I_8$ transition of Ho^{3+} can be deduced from the stronger J-mixing effect of $^5F_5$ energy level of Ho^{3+} with the application of high magnetic field intensity due to the larger angular momentum J of the $^5F_5$ energy level of Ho^{3+}.[22]

It is also interesting, as shown in Fig. 3A and C, that the upconversion luminescence intensity of the nanoparticles increases with increasing the magnetic field intensity. In order to understand the microscopic mechanism of the enhanced upconversion luminescence, we measured the absorption of lanthanide ions with NaYbF$_4$ and NaHoF$_4$ nanoparticles incorporated within the PDMS gel matrix (Fig. S3†). In the presence of magnetic field, the magnetic field induced energy level splitting of lanthanide ions might influence the absorption at the excitation wavelength (975 nm) and the upconversion luminescence intensity. To our surprise, the absorption intensity of lanthanide ions remains unchanged with increasing the magnetic field intensity (Fig. S3†), suggesting the absorption might not the main reason for the increasing luminescence intensity. On the other hand, the forbidden f–f transitions of lanthanide ions are sensitive to the local site symmetry, which can be distorted in the presence of magnetic field, as confirmed in the Eu^{3+} doped hexagonal NaYF$_4$.[16] However, the result shows the improvement of local site symmetry with

increasing the magnetic field intensity, which would decrease the upconversion luminescence intensity, indicating the change of local site symmetry is not the reason for the enhanced upconversion luminescence.

Because the absorption of Ho^{3+} and Yb^{3+} remains unchanged with the application of magnetic field (Fig. S3†), the energy resonance between $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+} and $^5I_8 \rightarrow {}^5I_6$ of Ho^{3+} might be little influenced by magnetic field. Due to the Zeeman effect, the broadening of upconversion luminescence from $^5F_4$, $^5S_2 \rightarrow {}^5I_8$, indicating the larger energy splitting of $^5F_4$, $^5S_2$, $^5I_8$ of Ho^{3+}, which might reduce the energy mismatch between $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+} and $^5I_6 \rightarrow {}^5F_4$, $^5S_2$ of Ho^{3+} with increasing magnetic field intensity. As the energy transfer from Yb^{3+} to Ho^{3+} plays an important role in the process of upconversion, we therefore believe that the energy transfer from Yb^{3+} to Ho^{3+} might be enhanced with increasing the magnetic field, resulting in the enhancement of the upconversion luminescence intensity from $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ and $^5F_4$, $^5S_2 \rightarrow {}^5I_7$ transitions.[33] Besides, the increasing population of $^5F_4$, $^5S_2$ of Ho^{3+} can increase the population of $^5F_5$ of Ho^{3+} for the multi-phonon relaxation from $^5F_4$, $^5S_2$ to $^5F_5$ of Ho^{3+}, resulting in the enhancement of upconversion luminescence from $^5F_5 \rightarrow {}^5I_8$ transition. On the other hand, the multi-phonon relaxation of Ho^{3+} from $^5I_6$ to $^5I_7$ might not much influenced by magnetic field for the larger J-mixing effect. The larger J-mixing effect of Ho^{3+} for the energy levels $^5I_7$ and $^5F_5$ (Fig. 3C) leads to a smaller
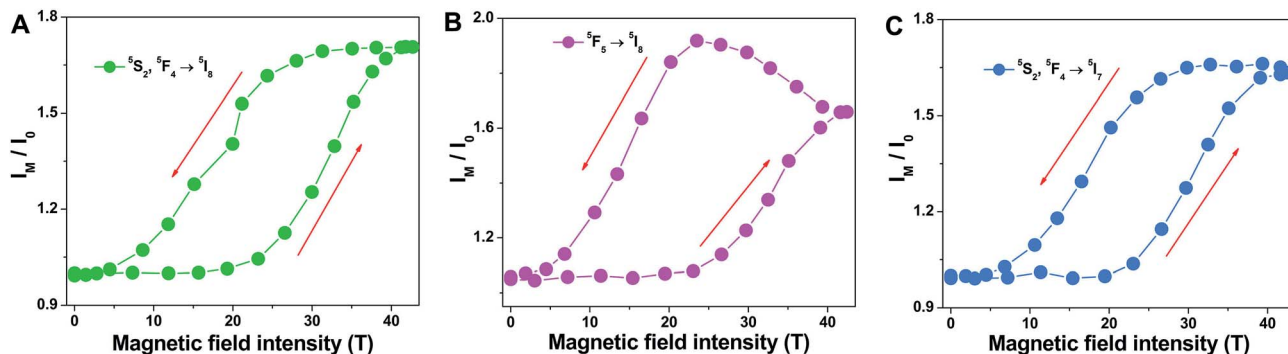
Fig. 4 Dependence of the ratio of integrated intensity of upconversion luminescence of $NaYF_4$: 20% Yb, 1% Ho nanoparticles from transitions of $^5F_4$, $^4S_2 \rightarrow {}^5I_8$ (A), $^5F_5 \rightarrow {}^5I_8$ (B), $^5F_4$, $^4S_2 \rightarrow {}^5I_7$ (C) of Ho^{3+} on different magnetic field intensities to those without the application of magnetic field. Arrows indicate the increase/decrease magnetic field intensity.

modification of the energy mismatch between $^5I_7 \rightarrow {}^5F_5$ of Ho^{3+} and $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+}. Therefore, the enhanced upconversion luminescence from $^5F_5 \rightarrow {}^5I_8$ transition is mainly originated from the enhanced energy transfer between $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+} and $^5I_6 \rightarrow {}^5F_4$, $^5S_2$ of Ho^{3+}. Therefore, the enhancement of upconversion luminescence from $^5F_4$, $^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$, $^5F_4$, $^5S_2 \rightarrow {}^5I_7$ transitions gives the similar behaviors in the process of increasing the magnetic field to 40 T, where the enhancement ratios (I_M/I_0) for $^5F_4$, $^5S_2 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$, $^5F_4$, $^5S_2 \rightarrow {}^5I_7$ transitions is 1.71, 1.69, 1.68, respectively.

By carefully compared with the luminescence spectra of nanoparticles at the same magnetic field intensity in the process of increasing and decreasing magnetic field (Fig. 3 and S4–S6†), we find obvious difference and mismatch in the spectra, suggesting the presence of magnetic–optical hysteresis behaviors (Fig. 4). In order to understand the nature of the magnetic–optical hysteresis behaviors of the upconversion luminescence, it is necessary to analysis the spin response of paramagnetic lanthanide ions to magnetic field. In a single pulse, the time for increasing magnetic field intensity from 0 T to 20 T is 4.59 milliseconds (ms) (Fig. S7†), that is, the "linear" rate for the increase of magnetic field is 4.36×10^3 T s^{-1}. The sudden change of magnetic field leads to the delayed spin flip of lanthanide ions and time dependent magnetization of nanoparticles and the upconversion luminescence of nanoparticles. Thus, the upconversion luminescence spectra recorded from 0 T to 20 T in the process of increasing magnetic field give the similar luminescence behaviors (Fig. 3A and C). Therefore, the delay spin response of lanthanide ions to the pulse magnetic field is responsible for the magnetic–optical hysteresis behaviors of upconversion luminescence intensity.

The magnetic–optical hysteresis behavior from the $^5F_5 \rightarrow {}^5I_8$ transition of Ho^{3+} in Fig. 4B seems abnormal as the maximum upconversion intensity appears at 23 T in the process of decreasing magnetic field intensity, while others at 40 T. This is because the stronger Zeeman effect at 40 T causes the larger energy levels splitting and promotes the phonon-assisted energy transfer for upconversion luminescence, resulting in the maximum luminescence intensity from $^5F_4$, $^4S_2 \rightarrow {}^5I_8$ and $^5F_4$, $^4S_2 \rightarrow {}^5I_7$ transitions (Fig. 4A and C). However, the energy level splitting for $^5F_5$ level of Ho^{3+} shows a similar behavior from

40 T to 20 T in the process of decreasing magnetic field (Fig. S8†) due to the strong J-mixing with magnetic field,[16] while energy level splitting for others is decreased during this process. The difference in the energy splitting of different Ho^{3+} levels at 23 T would probably reduce the energy mismatch between $^5I_7 \rightarrow {}^5F_5$ of Ho^{3+} and $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Yb^{3+} at 23 T, resulting in the enhanced energy transfer from Yb^{3+} to Ho^{3+} and upconversion luminescence at 23 T from $^5F_5 \rightarrow {}^5I_8$ transition of Ho^{3+}.

In conclusion, the upconversion luminescence of the hexagonal $NaYF_4$: Yb, Ho nanoparticles synthesized by co-precipitation method has been examined in the presence of a strong pulse magnetic field. Magnetic field enhanced upconversion luminescence of $NaYF_4$: Yb, Ho nanoparticles was observed for the first time, which is ascribed to the increasing energy transfer from Yb^{3+} to Ho^{3+} with increasing magnetic field intensity. The broadening of luminescence bands and splitting of luminescence peaks were also detected, originated from the Zeeman effect induced by magnetic field. Besides, the magnetic–optical hysteresis behaviors of the upconversion luminescence intensity for $NaYF_4$: Yb, Ho nanoparticles were observed, which can be explained in terms of the delayed spin re-orientation of paramagnetic lanthanide ions to magnetic field. The magnetic field enhanced upconversion luminescence might open a new road for improving upconversion efficiency.

Acknowledgements

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