Metal-enhanced upconversion luminescence of NaYF₄:Yb/Er with Ag nanoparticles

Zhaojin Wang^{1,2}, Chi Wang¹, Qingyan Han¹, Gang Wang¹, Mingdi Zhang¹,

Jing Zhang¹, Wei Gao¹ and Hairong Zheng^{1,*}

¹School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710119, PR China

²College of Physics and Optoelectronics Technology, Baoji University of Arts and Sciences, Baoji 721016, PR China

*Corresponding author: Hairong Zheng

E-mail: hrzheng@snnu.edu.cn

ABSTRACT

Single rare earth doped NaYF₄ nanoplate with different size of Ag nanoparticles is designed for the investigation of metal enhanced upconversion luminescence effect. Up to twice enhancement is obtained with big Ag nanoparticles. Luminescence quenching effect is also observed with small Ag nanoparticles. Exploration on the enhancement factors are carried out systematically based on the effect of local field enhancement, the coupling of LSPR with emission band, and even the enhanced far field distribution. It is suggested that the excitation enhancement is the reason for the enhancement at both wavelength. Emission enhancement also took a significant part in the result which is that in the system, the enhancement effect at 540 nm is greater than that at 650 nm.

Keywords: A. Optical materials, B. Chemical synthesis, B. Luminescence, B. Optical properties, C. X-ray diffraction

1. Introduction

Lanthanide-doped upconversion nanoparticles(UCNPs) have attracted much attention owing to their potential applications in biological imaging, solar cell, laser material and display technology[1-5]. However, UCNPs usually have low emission efficiency due to its small absorption coefficient of lanthanide ions[6-7]. Up to now, many strategies have been proposed to improve the luminescence property in order to enhance its intensity. These methods include matrix modification, introduction of dopant sensitizer, application of core/shell configuration, and metal enhanced fluorescence effect, etc[8-12]. Local surface plasmon resonance (LSPR) of noble metal nanostructure is considered as the origin of metal enhancement effect and is used to enhance upconversion(UC) luminescence efficiency[8-14]. Excitation field enhancement and emission field enhancement, which is resulted from the local field enhancement, are considered as two essential factors for obtaining metal enhanced fluorescence effect[15-20]. According to published study, results of experimental observation on the fluorescence enhancement are diversified and specific enhancement mechanism is still need to be investigated carefully. In most of experimental study, optical measurements are performed with ensemble of many particle system, for example in solution or powder system[21-27]. Therefore, it is necessary to establish a clear and effective system to investigate the fluorescence enhancement effect in a rather clear and precise manner.

In this paper, we use single NaYF₄:Yb/Er nanoparticle to study metal enhanced fluorescence with different size of Ag nanoparticles. The up-conversion luminescence emission of single composite nanoparticle is investigated with confocal microscopic

optical system. Obvious luminescence enhancement effect is obtained, which can be precisely repeated in experiments. We also use single NaYF₄:Yb/Tm nanoparticle to study metal enhanced fluorescence with 100 nm Ag nanoparticles. It is demonstrated that the emission enhancement probably is the main factor in UC luminescence enhancement process.

2. Experiment

2.1. Materials used for sample preparation

Y(NO₃)₃, Yb(NO₃)₃, Er(NO₃)₃ and Tm(NO₃)₃ are obtained by dissolving Y₂O₃, Yb₂O₃, Er₂O₃ and Tm₂O₃ in HNO₃ respectively. Original chemicals are from Sigma-Aldrich and the purity is 99.99%. NaF(98.0%), NaNO₃(99.0%), Na₃C₆H₅O₇·2H₂O(99.0%), (CH₂OH)₂(99.95%), AgNO₃(99.95%), and Polyvinyl Pyrrolidone(PVP) with analytical grade are supplied by Sinopharm Chemical Reagent Co., Ltd. (China).

2.2. Sample preparation

2.2.1 Synthesis of NaYF₄:Yb/Er and NaYF₄:Yb/Tm nanoplates

NaYF₄:Yb/Er nanoplates are synthesized with hydrothermal method mentioned in reference[28]. In the typical process of current study, 0.78 ml 0.5 mol/L of Y(NO₃)₃, 0.20 ml 0.5 mol/L of Yb(NO₃)₃, 0.02 ml 0.5 mol/L of Er(NO₃)₃ and 0.4800 g of Na₃C₆H₅O₇·2H₂O are dispersed in 35 ml DI water and mixed thoroughly to form chelate complex solution. Then, 2.2560 g NaNO₃ and 0.2820 g NaF are added into the solution and followed with stirring for 30 min to get white liquid. The white liquid is slowly transferred into a 50 ml Teflon-lined autoclave and is heated at 180 °C for 20

hours. After cooling down to room temperature naturally, the products are collected by centrifugation, washed with ethanol and DI water for several times, and finally dispersed in DI water for further use. For the NaYF₄:Yb/Tm nanoplates, the synthesis method and the quantity of chemicals used are the same, only convert Er(NO₃)₃ into Tm(NO₃)₃.

2.2.2. Preparation of Ag nanoparticles

Method used for synthesizing Ag nanoparticles is different for different particle size. For Ag nanoparticles with 20 nm dimension, the preparation process is as follow. Firstly, 200 mL of aqueous solution containing 45 mg AgNO₃ is prepared. Then 57 mg Na₃C₆H₅O₇·2H₂O in 5 ml DI water is added to the solution with stirring, which is then heated to boiling for 15 min with vigorously stirring[29]. After cooling down to room temperature naturally, the final product is centrifuged and washed with DI water for several times.

To get Ag nanoparticles with 100 nm in diameter, 100 ml (CH₂OH)₂ solution of PVP(1.25 g) is prepared first. Then 0.25 g AgNO₃ is added with stirring. The mixed solution is then heated to 130 °C for 15 min in oil bath with vigorously stirring. After cooling down to room temperature, the final products are centrifuged and washed with DI water for several times.

2.3. Assembling of NaYF₄:Yb/Er NPs with Ag nanoparticles

The solvent evaporation method is used to assemble NaYF₄:Yb/Er NPs with Ag nanoparticles. Firstly, NaYF₄:Yb/Er aqueous solution is prepared and dropped onto a clean silicon substrate surface. After dried at room temperature, Ag nanocrystal particle

solution is deposited onto it, which results in Ag nanoparticles at the surface of NaYF₄:Yb/Er nanoplate.

2.4. Sample characterization and spectroscopic measurement

The crystal structure of NaYF₄:Yb/Er nanocrystal plate is studied with X-Ray powder diffraction (Rigaku D/Max2550, Japan). The morphology of all particles and island substrate are characterized by scanning electron microscope (SEM, Nova NanoSEM 650) operating at a voltage of 20 kV. The Ag island substrate is deposited by electron beam evaporator (DE400). During the spectroscopic measurement, near infrared laser at 980 nm is employed as excitation light source. The spectrometer (SP2750i) equipped with charge-coupled device (CCD, ACTON) and photomultiplier tube (PMT, ACTON) detecting system is used for luminescence collection and detection. The confocal experimental setup is used with a modified optical microscope system (OLYMPUS-BX51). Magnification of the objective is 100 times, and the corresponding numerical aperture is 0.90. The laser beam spot size is around 1 μm. All of the spectroscopic measurements are carried out at room temperature.

3. Results and discussion

3.1. Sample characterization

The XRD measurement on the crystal structure of NaYF₄:Yb/Er nanoplates is presented in Fig. 1(a). Peaks in the XRD spectrum are well indexed as pure hexagonal NaYF₄ (JCPDS 16-0334). Fig. 1(c) and (d) are TEM images of 20 and 100 nm Ag nanoparticles. Fig. 1(e) and (f) are SEM images of NaYF₄:Yb/Er nanoplate with small and large Ag nanoparticles separately. The side length of hexagonal NaYF₄:Yb/Er

nanoplate is around 360 nm and its thickness is about 110 nm (Fig. 2(a)). The configuration of Ag particles around NaYF₄:Yb/Er nanoplate are clearly seen from the figure. The average diameter of Ag NPs is about 20 nm for small particles and 100 nm for large ones. Fig. 1(b) presents the absorption spectra of Ag nanoparticles. The absorption peaks of Ag NPs with diameter are 20 nm and 100 nm are located at 410 and 442 nm, respectively. The size distribution of Ag NPs is not very narrow, so the absorption spectra peak is broadened. For 100 nm Ag NPs, its absorption peaks appeared at the wavelength larger than 600 nm. Due to the creation of Ag NPs aggregates, plasmon resonances peaks will always appeared at larger wavelength[30-31].

3.2. Luminescence enhancement

The up-conversion luminescence emission of single composite nanoparticle is investigated with confocal microscopic optical system. The bright field image of single NaYF₄:Yb/Er nanoparticle is showed in Fig. 2(b), the dark field luminescence photographs of single NaYF₄:Yb/Er and NaYF₄:Yb/Tm nanoparticle are showed in Fig. 2(c) and (d). Fig. 3(a) shows UC luminescence emission spectra of NaYF₄:Yb/Er nanoplate with and without Ag NPs at the excitation wavelength 980 nm. Sharp characteristic spectral features are presented and spectral features keep similar in all spectra. Fig. 3(b) is schematic energy level diagram and possible transitions corresponding to Fig. 3(a). Emissions at 540 nm and 650 nm are from $^4S_{3/2} \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ respectively. Comparing with what observed from bare NaYF₄:Yb/Er nanoplate, the UC luminescence intensity from NaYF₄:Yb/Er with 20 nm Ag NPs is

slightly quenched while it is enhanced by 100 nm Ag NPs. For the sample with 100 nm Ag NPs, the luminescence intensity is increased by 2.0 and 1.5 times for 540 nm green emission and 650 nm red emission, respectively.

There are many factors in which may effect the metal enhanced luminescence effect. Local field enhancement including excitation and emission enhancement, energy transfer and non-radiative decay process are the mostly common considered reasons in understanding the mechanism of the enhancement[23]. To understand the observed experimental phenomena, it is necessary to study the property of the local EM field around the Ag particles through numerical simulation. Fig. 4(a) and (b) are electric field distribution around Ag nanoparticles under excitation of 980 nm laser, which is calculated with FEM simulation with surface plasmon oscillation. It can be regarded as large electric field can be built around 20 nm and 100 nm Ag sphere particles with light excitation. However, comparing the electric field around the 100 nm Ag particle with that around 20 nm Ag particle, the intensity of EM field is doubled at the distance of 23 nm from the surface of Ag sphere for 100 nm particle, and the enhanced EM field also distributes in a much broader space. For small Ag nanoparticle ($d=20$ nm), the enhanced electric field distribution is only within about 5 nm from the particle surface, which is more than 20 nm for 100 nm Ag particle. By consider the dimension of NaYF₄:Yb/Er nanoplate and the configuration of the sample system, it is not difficult to understand that the better luminescence enhancement will appear with bigger Ag nanoparticle.

For the luminescence quenching of the 20 nm Ag NPs samples, this may arise from

non-radiative decay due to the energy transfer process from excited state of Er^{3+} to Ag NPs. From the result of theoretical simulations above, we found the excitation field enhancement of Ag NPs with small size is not obvious, which indicates no-radiation decay plays a dominant role. In Fan Zhang's work[32], their research showed that small Ag particle($d=20$ nm) only weakly scatters and has the most narrow resonance near 400 nm, therefore having a low Sca/Abs value, and prefers quenching the RE emission. In contrast, large Ag particle($d=100$ nm) should have a relatively high Sca/Abs would be further beneficial for an enhanced excitation contribution. Their discussion are consistent with our experimental results.

To explore the mechanism behind the observed phenomena, the property of near local EM field distribution produced by LSPR are investigated carefully. Fig.4(c) present the simulated electric field distribution with the 100 nm Ag NPs around $\text{NaYF}_4\text{:Yb/Er}$ nanoplate under excitation of 980 nm laser. We calculate the average square of electric field enhancement factor with the following formula:

$$\frac{\oint (E/E_0)^2 dV}{V} \quad (1)$$

E_0 and E are the intensity of EM field without and with Ag NPs, V is the volume of the $\text{NaYF}_4\text{:Yb/Er}$ nanoplate. The average square of electric field enhancement factor is 1.35.

The UC luminescence emission from Er^{3+} peaks from $\text{NaYF}_4\text{:Yb/Er}$ nanoplate at the position that is away from the absorption spectral range of Ag nanoparticles. The system is good for investigating contribution of the field intensity to the enhancement effect, but it is not proper for studying the coupling of LSPR with the UC emission.

Considering the Tm^{3+} ion has UC emission at 453 and 474 nm is close to the peak position of LSPR, and the emission at 644 nm that is away from the LSPR, it is a ideal system for exploring the influence of LSPR on the emission process. Therefore, we substitute Er^{3+} by Tm^{3+} in the experimental system to investigate the enhancement effect of $\text{NaYF}_4:\text{Yb}/\text{Tm}$ nanoplate with 100 nm Ag NPs. Fig. 5(a) is the corresponding UC luminescence emission spectra observed experimentally. Similar enhancement effect is obtained under the same experimental condition. According to the transitions illustrated in the Fig. 5(b), energy transfer from Yb^{3+} to Tm^{3+} populates the $^3\text{H}_5$, $^3\text{F}_2$, $^1\text{G}_4$ and $^1\text{D}_2$ levels of Tm^{3+} , which leads to 453 nm ($^1\text{D}_2 \rightarrow ^3\text{F}_4$), 474 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_6$) and 644 nm ($^1\text{G}_4 \rightarrow ^3\text{F}_4$) emissions from Tm^{3+} . It should be pointed out the 474 and 644 nm emissions are from the same excitation level $^1\text{G}_4$. As presented in Fig. 5(a), the obtained enhancement factors for emissions of 453, 474 and 644 nm are 2.9, 2.2 and 1.7 respectively for the sample of $\text{NaYF}_4:\text{Yb}/\text{Tm}$ nanoplate with 100 nm Ag NPs. Enhancement effect of blue emission is slightly better because it has good spectral overlap with LSPR of Ag nanoparticles.

Because the LSPR absorption at the blue range is stronger than red, then the interaction or coupling with blue emission should be stronger than red. Thus, the enhancement factor at 474 nm emission is bigger than that at 644 nm. We noticed that 474 nm and 644 nm emissions are resulted from the same excitation energy level of $^1\text{G}_4$. If only the excitation enhancement exists, then enhancement factors of 474 and 644 nm emission should be similar. The enhancement difference observed experimentally shown in Fig. 5(a) indicates that both emission and excitation

enhancements are involved in the enhancement effect. The situation of spectral overlap and coupling effect determines the contribution of the emission and excitation enhancement.

In order to have further understanding of the coupling between UC nanocrystals and 100 nm Ag NPs, we studied the relation of radiation intensity and excitation power P . Fig. 6a and 6b present the pump power dependence of the luminescence intensity. Slops of 1.95 and 1.88 of the NaYF₄:Yb/Er NPs are obtained by linear fitting the experimental data for the green and red emissions, respectively. The slops are 1.57 and 1.68 for the green and red emissions respectively. When the NaYF₄:Yb/Er NPs are coupled with 100 nm Ag NPs. The result indicates that the green and red emissions from UCNPs are two photo excitation process[33-34]. In addition, we found that compared with the pure UCNPs, the slops of the UCNPs coupled with Ag NPs are decreased. This result indicate a more effective single photon upconversion process is involved, such as $^4I_{11/2} \rightarrow ^4F_{7/2}$ or $^4I_{13/2} \rightarrow ^4F_{9/2}$ transitions. It can be explained as the excitation field is enhanced by the Ag NPs and therefore there are more emitting state of Yb³⁺($^2F_{5/2}$) and Er³⁺($^4I_{11/2}$ and $^4I_{13/2}$). Some $^4I_{11/2}$ and $^4I_{13/2}$ of Er³⁺ can absorb a photon to reach high level such as $^4S_{3/2}$ and $^4F_{9/2}$ directly.

Moreover, we measure the UC luminescence lifetimes for NaYF₄:Yb/Er without and with 100 nm Ag NPs under 980 nm laser excitation. Fig. 7 is the luminescence decay process of the samples without and with Ag NPs. Bi-exponential function is employed for fulfill the data fitting[35]. The evolution of luminescence lifetime for $^4S_{3/2} \rightarrow ^4I_{15/2}$ (540 nm) transition are 66 and 54 μ s for the samples without and with Ag

NPs respectively. A shorter decay time is observed for samples with Ag NPs. The decrease of the lifetime means the increase of the radiative decay rate. In our experiment, we found that decay time decreased and the upconversion luminescence enhanced, so we think the corresponding radiation rate is increased.

The LSPR peak wavelength 430 nm is far from the excitation wavelength (980 nm). The average square of electric field enhancement factor is 1.35. Compared with the bare samples, the enhancement effect of 540 nm is better than that at 650 nm, the reason is that radiative decay rate of 540 nm increased, which is the effect of radiation enhancement. In addition, for the Tm^{3+} doped sample, slightly better enhancement effect is presented for blue emission than red emission. This also proves that good spectral overlap with LSPR of Ag NPs can increase the radiative decay rate. Therefore, the experimental data indicate the fluorescence enhancement by Ag NPs can be explained by the effect of the exciting enhancement of all wavelength and the increase of the radiative decay rate only at surface plasmon-coupled emission.

4. Conclusion

Rare earth doped NaYF_4 hexagonal nanostructures have been synthesized and metal enhanced luminescence system is prepared for single nanoplate with different size of Ag nanoparticles. UC emission and its enhancement effect are investigated systematically for single $\text{NaYF}_4\text{:Yb/Er}$ and $\text{NaYF}_4\text{:Yb/Tm}$ nanoplate with a confocal optical microscopy setup under 980 nm NIR excitation. The emission intensity of the nanoplate is modulated by Ag NPs. Bigger size Ag particles enhances the UC emission obvious, while small Ag nanoparticles quenches the UC emission slightly. The

maximum enhancement factor obtained in experiments is about 2 with 100 nm Ag NPs. The overall enhancement result depends on the metal particles size, as well as the spectral overlap of the LSPR and emission spectral property of the luminescence centers. It is suggested that the excitation enhancement is the reason for the enhancement at both wavelength. Emission enhancement also took an significant part to the result which is the enhancement effect at 540 nm is greater than that at 650 nm in the system. The results of the current work provide a novel approach for investigating the interaction between plasmonic system and upconverted luminescence system, which can lead to a deeper understanding of metal-enhanced luminescence effect.

Acknowledgements

The work is supported by the National Science Foundation of China (Grant 11574190, 11174190, 11304247 and 11604262), the Key Program of the Scientific Research of Baoji University of Arts and Sciences, China (Grant ZK11140), the Key Science and Technology Program of Shaanxi Province (Grant 2014K08-17), Scientific Research Program Funded by Shaanxi Provincial Education Department (Grant 15JK1043). Shaanxi Provincial Education Department (Program No.16JK1707).

References

- [1] E. Downing, L. Hesselink, J. Ralston, R. Macfarlane, *Science*. 276 (1996) 1185.
- [2] J. Sun, B. Xue, H. Du, *Opt. Commun.* 298(7) (2013) 37-40.
- [3] P. Dai, C. Li, X. Zhang, et al. *Light Science & Applications*, 5.2 (2016).
- [4] J. Yang, Y. Liu, D. Yan, et al. *Dalton Transactions* 45 (2016) 1364-1372.

- [5] F.Wang, Y. Han, C.S. Lim, Y.H. Lu, J.Wang, J. Xu, H.Y. Chen, C. Zhang, M.H. Hong, X.G. Liu, *Nature* 463 (2010) 1061.
- [6] W. Gao, H. Zheng, Q. Han, E. He, F. Gao, R. Wang, *J. Mater. Chem. C* 2 (2014) 5327-5334.
- [7] Z. Cheng and J. Lin, *Macromol. Rapid Commun.* 36 (2015) 790-827.
- [8] S. Schietinger, T. Aichele, H. Q. Wang, T. Nann, O. Benson, *Nano Lett.* 10 (2010) 134-138.
- [9] Y. Song, G. Liu, X. Dong, J. Wang, W. Wu, *J. Lumin.* 171 (2016) 124-130.
- [10] Z. Wang, W. Gao, R. Wang, et al., *Materials Research Bulletin* 83 (2016) 515-521.
- [11] H. Zhang, D. Xu, Y. Huang, X. Duan, *Chem. Commun.* 47 (2011) 979.
- [12] S. Schietinger, M. Barth, T. Aichele, O. Benson, *Nano Lett.* 9 (2009) 1694-1698.
- [13] J. Dong, Z. Zhang, H. Zheng, M. Sun, *Nanophotonics* 4 (2015) 472-490.
- [14] Z. Li, L. Wang, Z. Wang, X. Liu, Y. Xiong, *J. Phys. Chem. C*, 115 (2011) 3291-3296.
- [15] A. Priyam, N. Idris, Y. Zhang, *J. Mater. Chem.* 22 (2012) 960-965.
- [16] Q. Sun, H. Mundoor, J. Ribot, V. Singh, I. Smalyukh, P. Nagpal, *Nano Lett.* 14 (2014) 101-106.
- [17] Y. Ma, H. Liu, Z. Han, L. Yang, J. Liu, *Analyst*, 140 (2015) 5268-5275.
- [18] J. Shen, Z. Li, Y. Chen, X. Chen, Y. Chen, Z. Sun, S. Huang, *Appl. Surf. Sci.* 270 (2013) 712-717.
- [19] B. Zhou, B. Shi, D. Jin, X. Liu, *Nature Nanotech.* 10 (2015) 924-936.
- [20] G. Chen, C. Ding, E. Wu, B. Wu, P. Chen, X. Ci, Y. Liu, J. Qiu, H. Zeng, *J. Phys. Chem. C*, 119 (2015) 22604-22610.
- [21] A. Feng, M. You, L. Tian, S. Singamaneni, M. Liu, Z. Duan, T. Lu, F. Xu, M. Lin, *Sci. Rep.* 5 (2015) 7779.

- [22] D. Volpati, E. Spada, C. Cid, M. Sartorelli, R. Aroca, C. Constantino, *Analyst* 140 (2015) 476-482.
- [23] M. Fruhnert, F. Kretschmer, R. Geiss, I. Perevyazko, D. Cialla-May, M. Steinert, N. Janunts, D. Sivun, S. Hoeppener, M. Hager, T. Pertsch, U. Schubert, C. Rockstuhl, *J. Phys. Chem. C* 119 (2015) 17809-17817.
- [24] S. Cushing, J. Li, J. Bright, B. Yost, P. Zheng, A. Bristow, N. Wu, *J. Phys. Chem. C* 119 (2015) 16239-16244.
- [25] W. Stöber, A. Fink, E. Bohn, *J. Colloid. Interf. Sci.* 26 (1968) 62-69.
- [26] K. Sokolov, G. Chumanov, T. Cotton, *Anal. Chem.* 70 (1998) 3898-3905.
- [27] W.L. Lu, L.H. Cheng, H.Y. Zhong, J.S. Sun, J. Wan, Y. Tian, B.J. Chen, *J. Phys. D: Appl. Phys.* 43 (2010) 085404.
- [28] Q. Zhang and B. Yan, *Inorg. Chem.* 49 (2010) 6834-6839.
- [29] P.C. Lee, and D. Meisel, *J. Phys. Chem.* 86:17 (1982) 3391-3395.
- [30] E. Prodan, C. Radloff, N. Halas, P. Nordlander, *Science* 302 (2003) 419-422.
- [31] M. Schmeits, L. Dambly, *Phys Rev B* 44 (1991) 12706-12712.
- [32] F. Zhang, G.B. Braun, Y. Shi, et al. *Journal of the American Chemical Society*. 132 (2010) 2850-2851.
- [33] X. P. Chen, Q. Y. Zhang, C. H. Yang, D. Chen, C. Zhao, *Spectrochimica. Acta. Part. A*, 74 (2009) 441-445.
- [34] G. F. Wang, Q. Peng and Y. D. Li, *Chem. Eur. J.* 16 (2010) 4923-4931.
- [35] E. He, M. Moskovits, J. Dong, W. Gao, Q. Han, H. Zheng, N. Liu, *Plasmonics* 10 (2015) 357-368.

Figure

Fig. 1. (a) XRD pattern of as-prepared NaYF₄:Yb/Re(Re=Er, Tm), (b) UV-Vis absorption spectra of Ag nanocrystals. (c) TEM image of 20 nm Ag NPs, (d) TEM image of 100 nm Ag NPs, (e) to (f) SEM images of sample system with different assembly. (e) NaYF₄:Yb/Er with 20 nm Ag NPs, (f) NaYF₄:Yb/Er with 100 nm Ag NPs.

Fig. 2. (a) SEM images of $\text{NaYF}_4\text{:Yb/Er}$ ($\text{Re}=\text{Er, Tm}$), (b) The bright field image of single $\text{NaYF}_4\text{:Yb/Er}$ nanoparticle, (c) The dark field luminescence photograph of single $\text{NaYF}_4\text{:Yb/Er}$ nanoparticle, (d) The dark field luminescence photograph of single $\text{NaYF}_4\text{:Yb/Tm}$ nanoparticle.

Fig. 3. (a) Emission spectra of $\text{NaYF}_4\text{:Yb/Er}$ and $\text{NaYF}_4\text{:Yb/Er@Ag}$ (20 and 100 nm Ag NPs). The wavelength of the excitation light is 980 nm. (b) Energy level diagram with proposed UC mechanism for Er^{3+} and Yb^{3+} codoped NaYF_4 nanoparticles.

Fig. 4. Electric field distributions around Ag particles and island substrate under light excitation, the wavelength of incident light is 980 nm.

(a) 20 nm Ag sphere. (b) 100 nm Ag sphere. (c) 100 nm Ag NPs around NaYF₄:Yb/Er nanoplate.

The incident wave is linearly polarized, the polarization direction is along the x-axis and the propagation direction is along the z-axis.

Fig. 5. (a) Emission spectra of NaYF₄:Yb/Tm and NaYF₄:Yb/Tm with 100 nm Ag NPs. (b) Energy level diagram with proposed UC mechanism for Tm³⁺ and Yb³⁺ codoped NaYF₄ nanoparticles. The wavelength of the excitation light is 980 nm.

Fig. 6. Pump power dependence of the green and red UC intensity of the sample (a) NaYF₄:Yb/Er and (b) NaYF₄:Yb/Er@100 nm Ag NPs.

Fig. 7. Experimental results of time-resolved decay lines at 540 nm from NaYF₄/Yb,Er without and with 100 nm Ag NPs.