

Supplementary Information:

Multicolor Tunability and Upconversion Enhancement of Fluoride Nanoparticles by Oxygen Dopant

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Selection of Oxygen Source. Generally, there are several kinds of oxygen sources, including peroxy-acid, oxygen gas, metal oxide, and organic nitrogen oxide and nitrates. Because it is explosive at high temperature, peroxy-acid could not be used as the oxygen sources in the present system. The addition of metal oxide could pollute the inorganic NaGdF₄:Yb, Er UCNPs. Although oxygen gas was widely used as oxygen source, it is difficult to control the amount of oxygen in the present reaction system. Therefore, organic nitrogen oxides and nitrates with the relative high decomposition temperature were selected as oxygen sources. Among these organic nitrogen oxides and nitrates, ammonium nitrate (NH₄NO₃) is very cheap, and can decompose into nitrogen, oxygen and water when the temperature is higher than 230 °C (see below). This temperature is close to the thermolysis temperature of metal trifluoroacetate precursors (250 °C).

To examine the rationality of selecting NH₄NO₃ as oxygen source, we investigated the effects of different organic nitrogen oxide on the upconversion luminescent properties. Trimethylamine *N*-oxide and ammonium carbonate were selected as oxygen sources for comparing with NH₄NO₃, because they were used as oxygen transfer reagent. The control experiments showed that Yb, Er codoped fluoride UCNPs exhibited strong red emission of $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition, and the green emission band almost disappeared after addition of NH₄NO₃ (Fig. S1). While trimethylamine *N*-oxide and ammonium carbonate were used as oxygen sources, the strong green emission of $^4H_{11/2}$, $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions were shown. These results indicate that trimethylamine *N*-oxide and ammonium carbonate could not effectively manipulate the color output of Yb, Er codoped fluoride UCNPs. This may be due to the low oxygen atom content in trimethylamine *N*-oxide. There is no enough oxygen atom was formed after decomposition. And ammonium carbonate can be decomposed into CO₂ at low temperature, which may also not provide the oxygen atom to diffuse into the host matrix of fluoride UCNPs. The above results

revealed that the addition of NH_4NO_3 can effectively manipulate the color output of Yb, Er codoped fluoride UCNPs, and it is rational to use NH_4NO_3 as oxygen source.

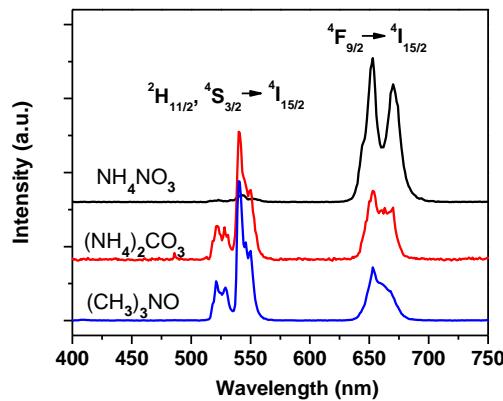


Fig. S1 Upconversion spectra of $\text{NaYF}_4:\text{Yb, Er}$ UCNPs prepared with various oxygen sources ($300\text{ }^\circ\text{C}$, 1h, $\text{NaYF}_4:\text{Yb,Er}$ 2 mmol). All of the UCNPs were excited at 980 nm with a 260 mW diode laser.

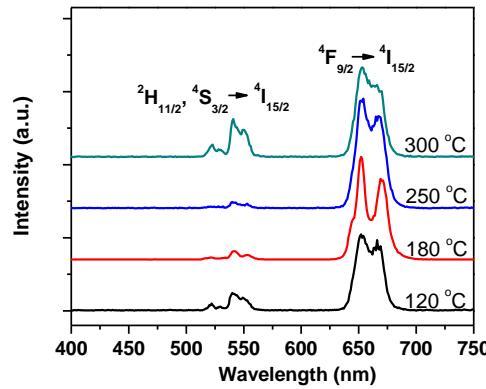


Fig. S2 Effect of addition temperature of NH_4NO_3 on the upconversion spectra of $\text{NaYF}_4:\text{Yb,Er}$ UCNPs (NH_4NO_3 20 mg per 2 mmol, $300\text{ }^\circ\text{C}$, 1h). All of the UCNPs were excited at 980 nm with a 260 mW diode laser.

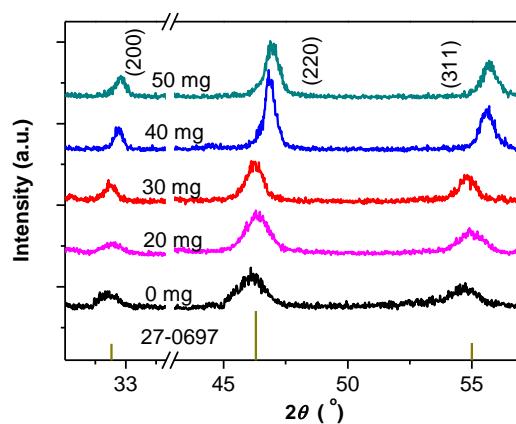


Fig. S3 Enlarged XRD patterns of NaGdF₄:Yb,Er UCNPs prepared with various amount of NH₄NO₃.

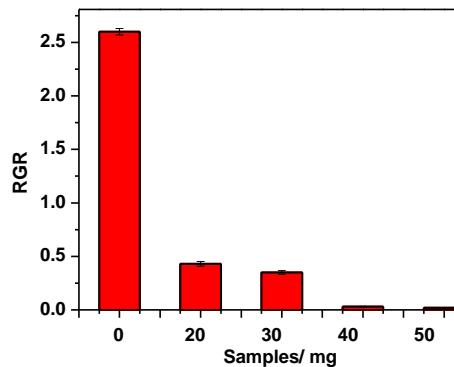


Fig. S4 Intensity ratios of green to red emissions of NaGdF₄: Yb,Er UCNPs prepared with various amounts of NH₄NO₃ per 2 mmol.

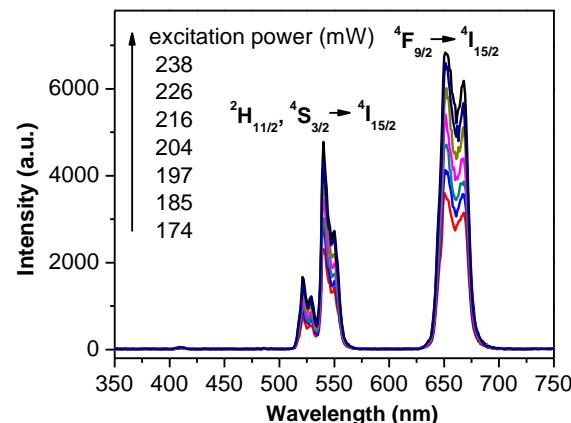


Fig. S5 Power dependence of upconversion spectra of NaGdF₄: Yb,Er UCNPs prepared at 300 °C for 1h, NH₄NO₃ 20mg.

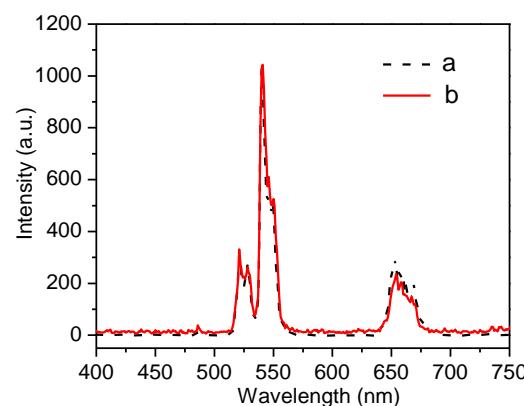


Fig. S6 Upconversion spectra of NaYF₄: Yb,Er UCNPs (2 mmol) with no addition of NH₄NO₃ (a) and the product after further reaction between as-prepared NaYF₄: Yb,Er and 50 mg of NH₄NO₃ at 300 °C for 1 h (b).

NH₄NO₃ and the prepared fluoride UCNPs with no oxygen impurities were added into reaction solution and reacted for 1 h at 300 °C, the results showed that the product was still in high green emission compared to the sample without addition of NH₄NO₃, implying that it is difficult to diffuse oxygen atom into host lattice of large-sized fluoride UCNPs.

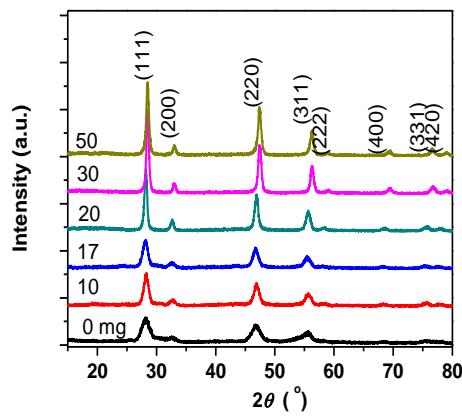


Fig. S7 XRD patterns of NaYF₄:Yb, Er UCNPs (2mmol) prepared with various amount of NH₄NO₃, 300 °C, 1h.

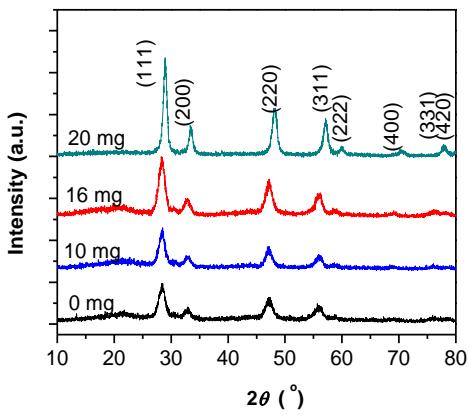


Fig. S8 XRD patterns of NLuF₄:Yb, Er UCNPs (2mmol) prepared with various amount of NH₄NO₃, 300 °C, 1h.

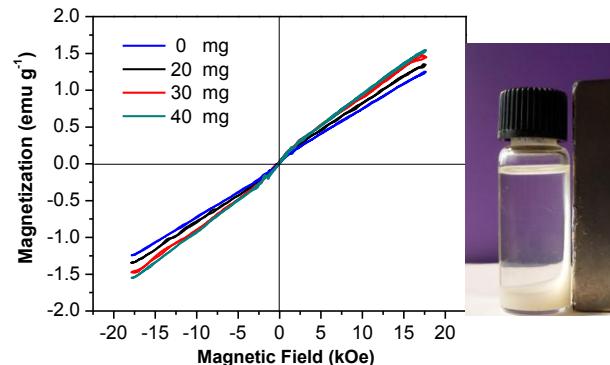


Fig. S9 Magnetization curves of NaGdF₄:Yb, Er UCNPs with various oxygen content.

Magnetic properties. Apart from upconversion luminescence, we also characterized the magnetic properties of the as-prepared NaGdF₄:Yb, Er UCNPs. Fig. S9 shows the magnetization curves of NaGdF₄:Yb, Er UCNPs with various oxygen contents. All the particles exhibit paramagnetism at room temperature. As oxygen contents increased, the magnetization of UCNPs increased from 1.25 to 1.5 emu/g at 20 KOe, which was close to the reported values of Gd-based nanoparticles^{1, 2}. It is revealed those NaGdF₄:Yb, Er UCNPs with multicolor output and proper paramagnetism can be further used for multi-mode applications.

REFERENCES:

1. Wang, Z. L.; Hao, J.; Chan, H. L. W. *J. Mater. Chem.* **2010**, *20*, 3178-3185.
2. Chen, D.; Yu, Y.; Huang, F.; Yang, A.; Wang, Y. *J. Mater. Chem.* **2011**, *21*, 6186-6192.