Supporting Information

Visualized NIR Obstacle Ranging Based on Upconversion nanoparticles

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EXPERIMENTAL SECTION

1. Materials

The reagents Erbium (III) chloride hexahydrate (ErCl$_3$·6H$_2$O), ytterbium (III) chloride hexahydrate (YbCl$_3$·6H$_2$O), yttrium (III) chloride hexahydrate (YCl$_3$·6H$_2$O), oleic acid (OA, ≥99.0%), 1-octadecene (ODE, >97.0%), methanol, absolute ethanol, sodium hydroxide (NaOH), ammonium fluoride (NH$_4$F) and sodium trifluoroacetate (C$_2$F$_3$NaO$_2$) were purchased from Aladdin Reagent (Shanghai). All chemical reagents were not further purified.

2. Synthesis of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ UCNPs

In a 100 mL three-necked flask, a mixture of RECl$_3$ (1 mmol), such as YCl$_3$ (0.5 mmol), YbCl$_3$ (0.49 mmol) and ErCl$_3$ (0.01 mmol), was combined with OA (6 mL), and ODE (14 mL). Then, the mixture was heated to 110 °C for 60 min to remove moisture, followed by heating at 150 °C for 30 min to completely dissolve the drugs encapsulated in OA. The solution was then cooled to 45 °C under a high-purity argon atmosphere. Subsequently, a methanol solution containing NaOH (2 mL) and NH$_4$F (6.6 mL) was rapidly injected into the reaction mixture, and the temperature was raised to 49 °C while stirring for 30 min. The temperature was further increased to 100 °C and maintained for 1 h to eliminate any residual methanol. The precursor was then heated to 305 °C and held under an argon atmosphere for 60 min to promote nucleation and crystallization. Finally, the product of UCNPs was collected by centrifugation at 8000 rpm for 5 min, followed by several washes with ethanol (3 mL) and cyclohexane (4 mL). The UCNPs were ultimately dispersed in 10 mL of cyclohexane.

3. Preparation of precursors

Na-TFA-OA precursors: To prepare a mixed solution, start by dissolving C$_2$F$_3$NaO$_2$ (4 mmol) in a small amount of methanol. After that, add as-obtained OA (10 mL) to the solution. Then it was kept at a normal temperature and vacuum environment for a whole day so that the methanol in the mixed solution was completely volatilized and then Na-TFA-OA precursors were successfully prepared.

Y-OA precursor: The preparation of yttrium chloride precursors (Y-OA) of oleic acid ligands mainly follows the following process. First, the as-obtained YCl$_3$ (2.5 mmol), OA (10 mL), and ODE (15 mL) were added to a 100 mL three-necked flask. Then the mixed solution was heated to 110 °C for 1 h under a high-purity argon atmosphere to remove moisture. After that, the temperature of the solution is raised to 150 °C for 30 min to produce a transparent colloid. Lastly, the temperature was dropped to 20 °C, the prepared Y-OA precursor was sealed in a glass bottle and stored in the refrigerator.

4. Synthesis of β-NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ core-shell structure:

The NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ UCNPs dispersed in cyclohexane were used as seeds to further grow the core-shell structure. The mixed solution of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ (2.5 mL), OA (4 mL) and ODE (6 mL) was added to a 100 mL three-necked flask. Next, the mixture was heated to 110 °C for 60 min to remove moisture, and then heated up to 270 °C with condensation reflux, followed by three slow injections of Y-OA precursor (4 mL) and Na-TFA-OA (2 mL) in three divided doses over 3 h, and then cooled to room temperature. Last, the UCNPs product was collected by centrifugation at 8000 rpm for 5 min and washed several times by adding ethanol (3 mL) and cyclohexane (4 mL). The UCNPs were dispersed in 4 mL cyclohexane for subsequent measurement and use.

5. Characterization:
Observe the morphology, size, and spacing of UCNPs lattice fringes using transmission electron microscopy (TEM, JEM-F200). UCL is measured by an external 980 nm zoom laser on a fluorescence spectrometer (HITACHI-F7000) equipped with a xenon lamp and an ocean optical fiber spectrometer. The X-ray diffraction (XRD) pattern was measured on the TD-3500 X-ray diffractometer of Dandong Tongda Technology Co., Ltd. All optical photos were taken by the digital camera of Nikon D7100 with AF-S Micro-Nikkor 105 mm f/2.8G IF-ED at room temperature.
Figure S1. (a) UCL spectra of the NaYF₄: x%Er³⁺, (1 - x) %Yb³⁺@NaYF₄ (x = 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6) UCNPs. (b) UCL emission intensities of NaYF₄: Yb³⁺, Er³⁺@NaYF₄ UCNPs at 541 and 657 nm as a function of the concentration of Er³⁺.
Figure S2. Characteristic peak intensity of power-dependent UCL spectra of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$ UCNPs.
**Figure S3.** CIE coordinates diagram of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ UCNPs as a function of pump density.
The proposed discoloration mechanism of the NaYF₄: Yb³⁺, Er³⁺@NaYF₄ UCNPs is mainly influenced by the cross-relaxation process between ions and the reverse energy transfer process, both of which have been reported in relevant literature¹⁴, as is shown in Figure S9. When the UCNPs are excited by 980 nm laser, the UCL of UCNPs is affected by the cross-relaxation (CR) and reverse energy transfer (BET) processes. With the increase of power density, the processes of CR₁, CR₂ and CR₃ are significantly inhibited, while promoting the BET process between Yb³⁺ and Er³⁺, as previously reported as Berry, M. T.⁵ This BET process promotes the population of Er³⁺ excited states, resulting in enhanced red emission and weakened green emission, ultimately resulting in a change in luminous color from green to red.

Figure S4. UCL mechanism of the NaYF₄: Yb³⁺, Er³⁺@NaYF₄ UCNPs.
Figure S5. Stability of temperature. (a) Plot of the integrated intensity ratio of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ UCNPs as a function of pump density. (b) Plot of the integrated intensity ratio of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ UCNPs as a function of distance. (c) Photographs of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ UCNPs as a function of pump density. (d) Photographs of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ UCNPs as a function of distance.

In order to investigate the potential influence of temperature, we monitored the temperature of the sample solution when stimulated by the 980 nm collimating laser with different power levels and the 980 nm zoom laser at different distances, as presented in Figure S8. It can be observed that the temperature of the solution remains stable by changing the distance, indicating that the color change observed in the UC particles is independent of thermal effects.
Figure S6. Basic application of laser obstacle ranging. (a) Range model of 980 nm laser obstacles. (b) UCL spectra of NaYF$_4$: Yb$^{3+}$, Er$^{3+}$@NaYF$_4$ without obstacle. (c) Plot of the integrated intensity ratio of $I_{541\text{ nm}} / I_{657\text{ nm}}$ as a function of distance with obstacle.

Since the ranging method utilized in this manuscript is based on the color change of nanoparticles, specifically the alteration in the red-green ratio of upconversion luminescence, as depicted in Figure S4c. The range sensitivity is closely related to the variation of red-green ratio. According to the test in the experiment, the red-green ratio of PL spectrum is in a dynamic state, meaning there is no fixed value of distance sensitivity. However, it is worth noting that a higher degree of change in the red-green ratio of PL spectrum corresponds to a smaller distance sensitivity. Conversely, a smaller variation in the red-green ratio of the PL spectrum results in a greater range sensitivity in the measurement.
Figure S7. Absorption spectra of different objects.
Figure S8. Absorption spectra of different obstacles. (a) Pork slice. (b) Pig skin. (c) Leaf. (d) Orange peel. (e) Test barrier. (f) Wood.

The obstacles can absorb a certain amount of NIR light, which can result in different colors being observed at certain distances, as shown in Figure 4c. This is because the presence of obstacles can introduce variations in the PL spectra due to the absorption effect on the laser, and then affect the accuracy of obstacle ranging. Besides, the absorption can vary between different objects, as shown in the Figures S5 and S6. According to reports, in order to make the ranging more accurate, researchers have also proposed many methods to calibrate the rangefinder, such as 2023 Mohammadamin Manouchehri et al proposed three different external efficiency methods in order to obtain more accurate external parameters. Yu Haoyang et al. introduce a self-calibration technique that can extract secondary sampling repetition rate information directly from interferogram (IGM), providing a cost-effective scheme for high-performance absolute distance measurement. Tu Yuhong et al. proposed a novel external calibration method to obtain accurate and stable calibration results of the combined camera-1D laser rangefinder sensor, so as to perform external calibration of the stability of the ranging. Therefore, during the ranging process, we firmly believe that employing the correct calibration method can effectively optimize ranging performance and keep the results in control. For example, when using a leaf as an obstacle, a systematic approach can be followed to ensure accurate measurements. First, the absorption spectra of multiple leaves can be measured to identify leaves with minimal laser absorption at 980 nm laser. These leaves should be selected as calibration standards for obstacle ranging. Once the optimal leaves are selected, several measurements can be conducted to determine the best position of the leaf during the measurement process. This involves placing the leaf at different distances from the NIR-based UC nanoparticles and recording the emission colors (or I_{541}/I_{657} nm ratios) at each distance. The position that consistently yields the most accurate and reliable measurements can be considered the optimal position for obstacle ranging with leaves. Additionally, to ensure consistency and reliability in subsequent tests, it is important to maintain a consistent surrounding environment.
Calculation of the relationship between the distance between the laser and the sample and the red-to-green ratio of UCL: In order to accurately determine the relationship between the measured distance and the variation in red-to-green ratio of UCNP luminescence, various fitting methods such as linear regression and nonlinear regression were employed to fit the following formula.

\[ y = 0.000148x^2 - 0.00262x + 0.09104 \]

Equation is the fitting curve formula of \( \frac{I_{541\text{ nm}}}{I_{657\text{ nm}}} \). The experimental distance information is obtained by calculating based on this formula, enabling a comparison with the theoretical values. This yields the measurement error data presented in Figure S10.
References


