Supporting Information

Near-White-light emissive upconversion nanoparticles $NaYF_4$:50%Yb,2%Er@$NaYbF_4$:1%Tm @$NaYF_4$ for the ratiometric fluorescence detection of sulfite

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Experimental

Materials.

Yttrium oxide (Y_2O_3, 99.99%), ytterbium oxide (Yb_2O_3, 99.9%), erbium oxide (Er_2O_3, 99.5%), thulium acetate ($Tm(Ac)_3$, 99.9%), sodium oleate (NaOA, 98%) and sodium trifluoroacetate (Na-TFA, 97%) were purchased from Shanghai Macklin's Biochemical Technology Co., LTD. 1-octadecene (ODE, 90%), oleic acid (OA, AR), and oleylamine (OM, 70%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Ammonium fluoride (NH_4F, >96%), cyclohexane (AR), sodium sulfite (Na_2SO_3, AR), PAR, tannin, glucose, sodium chloride (NaCl), potassium bromide (KBr), sodium hyposulfite ($Na_2S_2O_3$), sodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium acetate (NaAC), ascorbic acid (AA) and sodium sulfate (Na_2SO_4) were purchased from Chengdu Kelong Chemical Co., LTD. Anhydrous ethanol was purchased from Chengdu Jinshan Reagent Co., LTD. All chemicals are used directly without further purification.

$LnCl_3$ (Ln=Yb, Er and Y) were obtained by dissolving their corresponding metal oxides with hydrochloric acid and then evaporating the water completely.

Characterization.

Powder X-ray diffraction (XRD) data were obtained using a Shimazu XRD-6100 diffractometer with Cu-Ka radiation (λ= 1.5406 Å) at 40 kV and 30 mA. The morphology and size of the as-prepared UCNPs were determined on JEOL 2100 Plus transmission electron microscopy (TEM). The upconversion luminescence emission spectra were recorded on F-7000 fluorescence spectrophotometer, which attached to a 980 nm laser (MDL-XF-980-10W) purchasing from Changchun New Industry. Unless otherwise specified, the test conditions were as follows (concentration: 10 mg/mL; solvent: cyclohexane). Notably, the upconversion emission spectra (Figure 1f) of the core, the core-shell and the core-shell-shell of NWL-UCNPs are excited at 4000, 800 and 160 W/cm^2, respectively. And the "P" in the paper stands for excitation power. The ultraviolet-visible (UV-vis) absorption spectra were obtained on a U-2900 ultraviolet–visible spectrophotometer.

Synthesis of $NaYF_4$:50%Yb, x%Er cores (x=0.5, 2, 10).

A mixture of $YbCl_3$ (1 mmol), YCl_3(0.99/0.96/0.8 mmol), $ErCl_3$(0.01/0.04/0.2 mmol), OA (18.25 mL), and ODE (20 mL) was put in a 100 mL three necked flask. The flask was stirred under vacuum and heated to 110 °C for 1 h. 6.25 mmol of sodium oleate, 0.01 mmol of NH_4F, 6.25 mL of oleyl amine and 8.75 mL of ODE were added after the flake cooled to 30 °C. The flask was placed in a vacuum again and stirred at room temperature for 30 min. Then, the flask was heated rapidly to 315 °C in a nitrogen atmosphere for 45 min. After rapid cooling, the reactant was transferred to five centrifuge tubes containing 200 mL anhydrous ethanol to be precipitated the nanoparticles and then centrifuged at 7500 rpm for 10 min. Subsequently, the white products were dispersed in 25 mL of cyclohexane and then centrifuged and washed with ethanol. Finally, the nanoparticles were dispersed in 50 mL of cyclohexane.

Synthesis of $NaYF_4$: x%Yb,2%Er cores (x=25, 50, 98).

Synthesis of the $NaYF_4$: x%Yb,2%Er cores UCNPs (x=25, 50, 98) was similar to the above procedures, but the lanthanide chloride was changed accordingly. 1.46 mmol of YCl_3, 0.04 mmol of $ErCl_3$ and 0.5 mmol of $YbCl_3$ were used for $NaYF_4$:25%Yb,2%Er core. 0.96 mmol of YCl_3, 0.04 mmol of $ErCl_3$ and 1 mmol of $YbCl_3$ were used for $NaYF_4$:50%Yb,2%Er core. 0.04 mmol of $ErCl_3$ and 1.96 mmol of $YbCl_3$ were used for $NaYbF_4$:2%Er core.

Preparation of shell precursors.

0.1 mol/L OA-Ln: 4 mmol of lanthanum chloride (Ln=Y, Yb) or thulium acetate ($Tm\ (Ac)_3$), 16 mL of OA, and 24 mL of ODE were added to a 50 mL three necked flask. The flask was stirred vigorously under vacuum and slowly heated to 110 °C for 15 min and then the temperature was fixed at 160 °C until dissolved.

0.4 mol/L Na-TFA-OA: 45 mL of OA and 18 mmol of sodium trifluoroacetate were added to a 100 mL flask. The solution was vigorously stirred under vacuum at room temperature until dissolved.

Synthesis of $NaYF_4$:50%Yb,2%Er@$NaYF_4$:x%Yb,1%Tm@$NaYF_4$ UCNPs by using the successive layer-by-layer (SLBL) method (x=0, 10, 30, 60, 99).

Stock $NaYbF_4$ core nanoparticles (2.7 mL), OA (4 mL) and ODE (6 mL) were added into a 50 mL flask and stirred violently under vacuum and was heated to 70 °C for 30 min. Nitrogen gas was introduced all the time and the mixture was heated at 300 °C for 5 min, before the injection table below was followed (Table S1). Each cycle included injections of Ln oleate solution with a waiting time of 15 minutes and sodium trifluoroacetate solution. The first four cycles were carried out to fabricate the middle shell, and the last four cycles were to fabricate the inert shell. In each cycle of middle shells, the proportion of Yb, Y and Tm was x%, (99-x) % and 1%, respectively. In each cycle of inert shells, the proportion of Y was 100%. After being held at 300 °C for 30 min, the flask was rapidly cooled to 75 °C and centrifuged at 7500 rpm for 10 min after adding 30 mL anhydrous ethanol. The nanoparticles were dissolved in 5 mL cyclohexane, added with 35 mL of anhydrous ethanol and centrifuged at 7500 rpm for 10 min. Finally, the nanoparticles were dissolved in cyclohexane (5 mL).

Table S1: Shell precursor injections

Cycle number	1	2	3	4	5	6	7	8
Ln-OA (mL)	0.28	0.36	0.44	0.52	0.62	0.72	0.83	0.95
Na-TFA-OA (mL)	0.14	0.18	0.22	0.26	0.31	0.36	0.42	0.48

Surface modification of NWL-UCNPs

The coating of oleic acid (OA) ligands on the surface of UCNPs makes the prepared UCNPs hydrophobic, which is not conducive to its application in solution environment. Therefore, an exchange ligand treatment was performed using $NOBF_4$ and PAA to impart hydrophilicity. Specifically, 5 mL of NWL-UCNPs dispersed in cyclohexane was firstly added to 5 mL of N, N-Dimethylformamide (DMF). Subsequently, 0.05 mmol $NOBF_4$ solids were added and stirred for 60 min. Then the mixed solution was transferred to a centrifuge tube and centrifuged at 12000 rpm for 20 min, the product was dispersed in H_2O (5 mL). Afterward, 3 mL 50 mg/mL PAA aqueous solution was added to the above aqueous solution and magnetically stirred at room temperature for 24 h. Finally, the mixed solution was transferred to a centrifuge tube and centrifuged at 12000 rpm for 20 min and the hydrophilic NWL-UCNPs were redispersed in H_2O (5 mL).

UCL nanoprobes for sulfite detection

To prepare a sensitive detection for sulfite, a composite nanoprobe combining NWL-UCNPs and PAR was introduced. Firstly, 50 μL of NWL-UCNPs stock solution was added to a cuvette and diluted to 1976 μL with Britton-Robinson (BR) buffer solution (5 mM, pH = 6.80). Subsequently, 24 μL of a 5 mM PAR aqueous solution was added to the above solution to prepare the composite probe solution for sulfite detection. In this solution, the concentration of PAA-$NOBF_4$-NWL-UCNPs was calculated to be 0.25 mg/mL, and the concentration of PAR was 60 μM. Then, 2 μL of certain concentrations of Na_2SO_3 solution was added to the probe solution for detection, where the final concentration of Na_2SO_3 was 0, 1, 5, 10, 20, 30, 50, 70, 90, 110, 130, 150 μM, respectively. Finally, the probe solution was excited under 980 nm excitation (398 W/cm^2), and the UCL spectra in the range of 400-800 nm were recorded. For absorbance analysis of sulfite, absorption spectra of the probe solution were tested in the range of 400-800 nm. In terms of selectivity testing, the luminescent response of the UCL nanoprobe to other interferents was studied through the same testing procedure, and the concentration of other interferents is 10 times that of sulfite.

Practical application of the UCL sensor.

To assess the practical sensing performance of the sensing platform, four different samples (rice wine, canned yellow peach, vermicelli and red wine from the Great Wall brand) were chosen. 2.5 g vermicelli was taken in a 50 ml volumetric bottle, filled with BR buffer solution. Rice wine, canned yellow peach and red wine were diluted 20-fold using BR buffer solution. The concentration of the four samples was then analyzed using the previously described detection procedure. Additionally, the recovery of the sensing platform was calculated by adding quantitative sulfite ions (0, 50, 100 μM) to the samples, and each experiment was repeated three times.

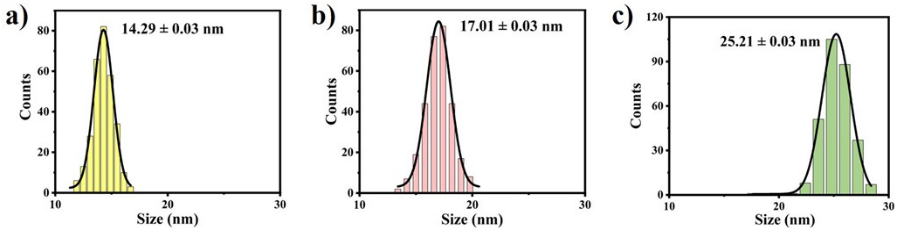

Figure S1. Size distribution of the core (a), the core-shell (b), and the core-shell-shell (c) of NWL-UCNPs (N = 300 nanoparticles).

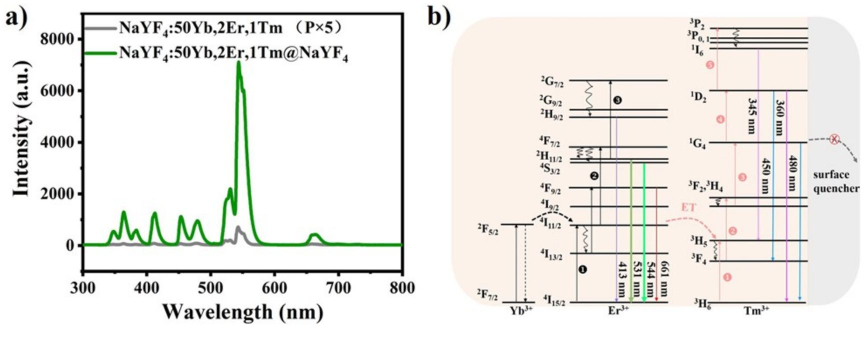

Figure S2. Upconversion emission spectra (a) of the NaYF$_4$:50%Yb,2Er,1%Tm and the NaYF$_4$:50%Yb,2Er,1%Tm@NaYF$_4$ UCNPs under 160 W/cm^2. Energy level diagram (b) of the NaYF$_4$:50%Yb,2Er,1%Tm@NaYF$_4$ UCNPs.

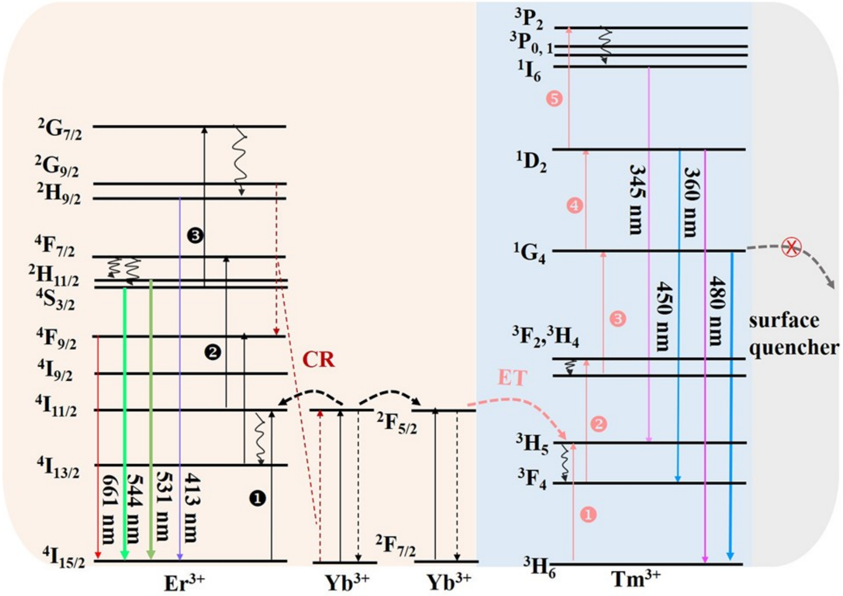

Figure S3. Energy level diagram of $NaYF_4$: 50%Yb, 2%Er@$NaYF_4$: 1%Tm@$NaYF_4$ under 160 W/cm^2 excitation.

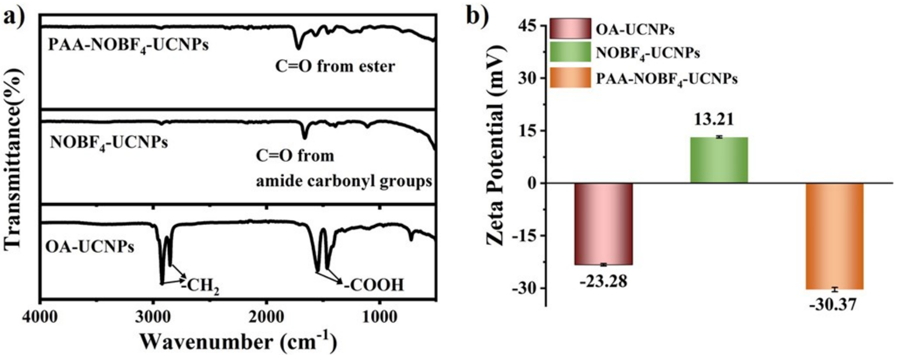

Figure S4. FT-IR spectra and Zeta potential analysis of OA-UCNPs, $NOBF_4$-UCNPs and PAA-$NOBF_4$-UCNPs.

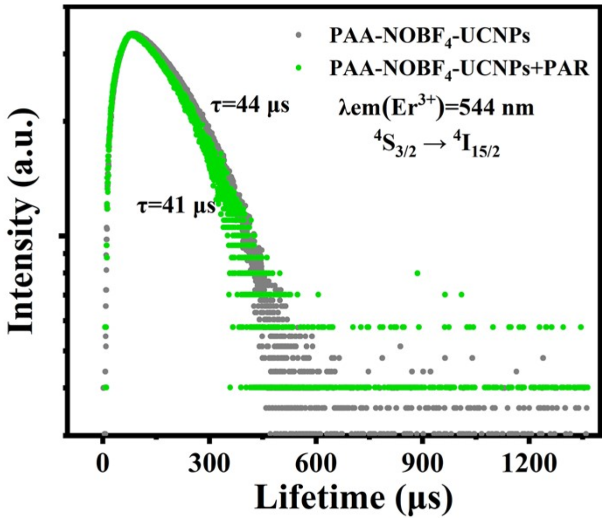

Figure S5. The decay curves of the emission of PAA-NOBF$_4$-UCNPs at 544 nm in the presence and absence of the PAR.

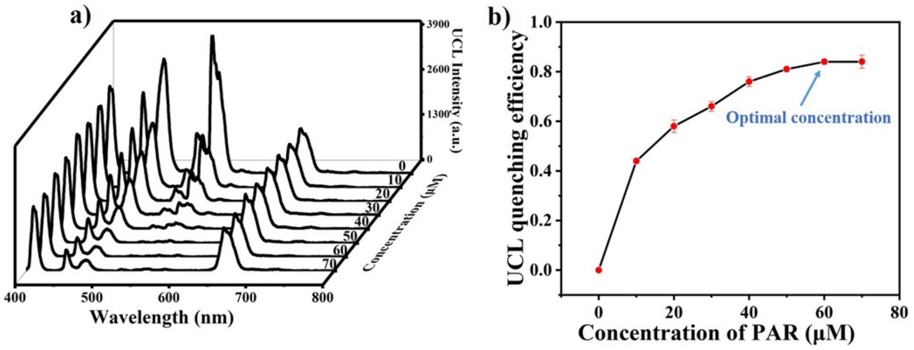

Figure S6. Upconversion emission spectra (a) of UCNPs with the addition of varying concentrations of the PAR. Quenching behavior (b) of UCL with increasing concentrations of the PAR agent.

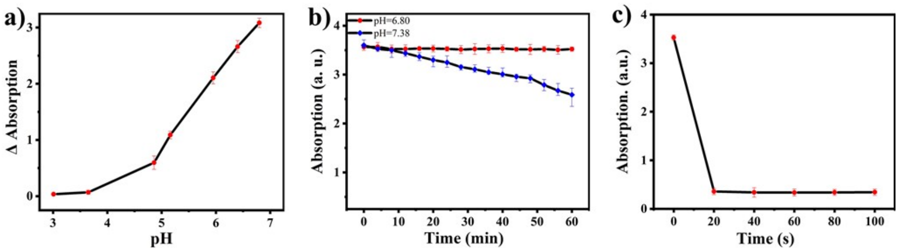

Figure S7. Optimization of detection conditions: (a, b) pH, dynamic response (c) after the addition of 150 μM sulfite.

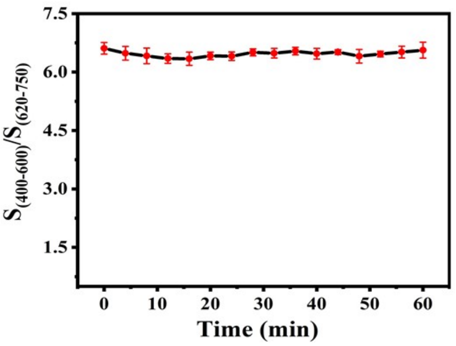

Figure S8. Effect of time on the S $_{(400-600)}$/S $_{(620-750)}$ of the upconversion nanoprobe with the addition of 150 μM sulfite.

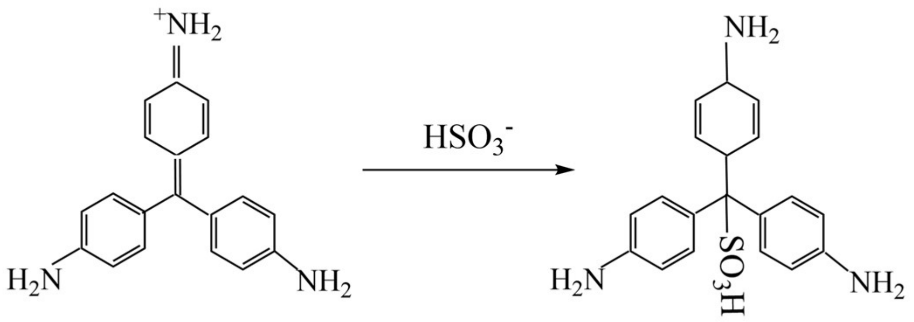

Figure S9. Reaction mechanism diagram of PAR and HSO_3^-.

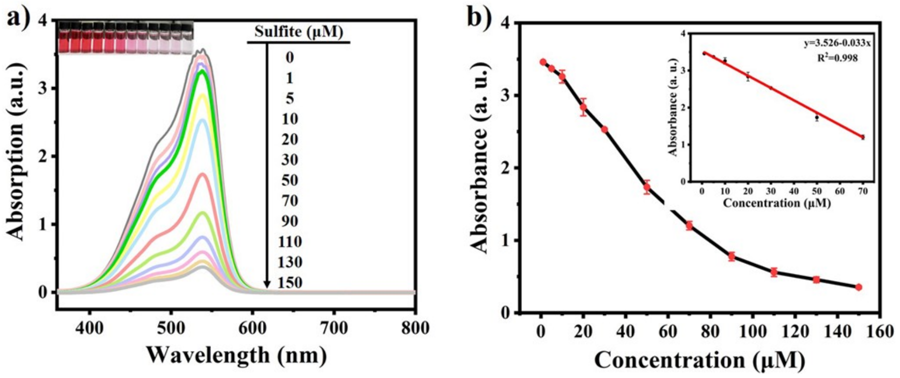

Figure S10. UV-vis absorption spectra evolution (a) of PAR as sulfite concentration increases. The relationship (b) between PAR absorption and sulfite concentration.