Supporting Information

Upconversion Nanoparticles for Ratiometric Fluorescence Detection of Nitrite

Junfen Han,^{ab}Cheng Zhang,^{ab}Fei Liu,^cBianhua Liu, ^{*b}Mingyong Han,^bWensheng Zou,^bLiang Yang,^{ab} Zhongping Zhang^{*ab}

^a Department of Chemistry, University of Science & Technology of China, Hefei, Anhui 230026,

China

^b Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, Anhui 230031, China

^c Fujian Inspection and Research Institute for Product Quality, Fuzhou, Fujian 350002, China

* To whom correspondence should be addressed. <u>bhliu@iim.ac.cn</u>; zpzhang@iim.ac.cn

Effect of reagents

The certain experimental conditions are investigated in details.

The effect of the volume of HCl on the reaction of NO_2^- and NR was studied and the results are shown in Figure S6. It can be seen that when the volume of HCl (1.0 M) is 60 μ L, the reaction is complete. So 60 μ L of HCl is recommended for use in the assay.

Then we studied the time of reaction, it can react completely in 10 min and maintains unchanged more than 30 min. These results are shown in Figure S7.

At last, the volume of the upconversion luminescence nanoparticles was studied in this paper. As shown in Figure S8, with the volume of PAA-capped UCNPs (10 mg/mL) increasing, the turn on efficiency also increases slightly. Considering of the sensitivity and linear range, 25 μ L of PAA-capped UCNPs is chosen in the article.



Figure S1. (A) HR-TEM image of the NaYF₄:Yb(20%),Er(2%) nanoparticles. (B) Comparison of X-ray diffraction pattern of the UCNPs samples and the standard hexagonal NaYF₄ (JCPDS no. 16-0034).



Figure S2. TEM image of the as-prepared PAA-capped NaYF₄:Yb(20%),Er(2%) nanoparticles.



Figure S3. FT-IR spectra of the NaYF₄:Yb³⁺,Er³⁺ nanoparticles before (top line) and after (bottom line) ligand-exchange using poly(acrylic acid) (PAA); After ligand exchange by PAA, the obvious peak at 1732 cm⁻¹ suggests the presence of the -COOH groups on surface of the nanoparticles.



Figure S4. The pH-dependent UV-vis absorption spectra of the formed diazonium salt in different pH values of 2.0, 3.0, 4.0, 5.0 and 6.0.



Figure S5. The ratios of upconversion luminescence intensity (I_{539}/I_{654}) versus the amount of neutral red (NR).



Figure S6. Effects of the volume of HCl (1.0 M) on the absorption of NR (210 μ L, 1.0 mM). The concentration of NO₂⁻ is 62.5×10⁻⁵ M and the reaction time is 10 min.



Figure S7. Effects of the reaction time on the absorption of NR (210 μ L, 1.0 mM). The concentration of NO₂⁻ is 62.5×10⁻⁵ M and the volume of HCl (1.0 M) is 60 μ L.



Figure S8. The luminescence intensities of PAA-capped NaYF₄:Yb³⁺,Er³⁺ in the absence (a) and presence (b) of NO₂⁻ (62.5×10^{-5} M) and increasing efficiency (c) against the volume of UCNPs (10 mg/mL). The volume of NR (1.0 mM) is 210 µL and HCl (1.0 M) is 60 µL.



Figure S9. The evolution of UV-vis spectra of 210 μ L neutral red (1.0 mM) with the increase of NO₂⁻ concentration. The inset shows the calibration curve corresponding to the absorption intensity of neutral red at 525 nm *versus* the concentrations of NO₂⁻.



Figure S10. The calibration curve corresponding to the upconversion luminescence intensities at 539 nm *versus* the concentrations of NO_2^- .



Figure S11. The calibration curve corresponding to the hue (digital color tone) versus the concentrations of NO_2^- .



Figure S12. Selectivity (black bar) and interference test (red bar). The selectivity data were obtained using 62.5 mM cations/anions and 62.5×10^{-5} M NO₂⁻. The anti-interference tests were performed by the addition of 62.5×10^{-5} M NO₂⁻ in the coexistence of an excess of interfering ions (62.5 mM).