Electronic Supplementary Information

Selective antenna effect of tungstate anion for Tb-doped layered yttrium

hydroxynitrate

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Experimental details

1. Synthesis of Tb-doped layered yttrium hydroxynitrate

Tb-doped layered yttrium hydroxynitrate $(Y_{1.90}Tb_{0.10}(OH)_5NO_3 nH_2O; LYH:Tb)$ was synthesized via a hydrothermal reaction. Typically, Y_2O_3 (2.0 g) and Tb_2O_3 (0.1706 g) were dissolved in HNO₃ (10%, 40 mL) solution with slight heating. After clear solution was formed by uniform stirring, aqueous KOH (10%) solution was dropwise added with vigorous stirring at room temperature until the pH of solution was adjusted to approximately 6.9. The resulting solution was then put into a Teflon-lined stainless steel autoclave with a capacity of 100 mL. The autoclave was sealed and maintained at 135 °C for 18 hr. The solution was continuously stirred during the hydrothermal treatment. After the reaction was completed, the solid product was collected by filtration, washed with distilled water, and dried at 60 °C for a day.

2. Adsorption of metal-oxoanions on LYH:Tb

For the adsorption of metal-oxoanions, test aqueous solutions $(10^2 \text{ and } 10^4 \text{ ppm})$ were prepared by dissolving Na₂WO₄·2H₂O, K₂CrO₄, Na₂MoO₄·2H₂O, Na₃VO₄, and NaVO₃ in deionized waters at room temperature. LYH:Tb powder (200 mg) was added to 20 mL of 10^2 ppm and 10^4 ppm aqueous tungstate (WO₄²⁻), molybdate (MoO₄²⁻), chromate (CrO₄²⁻), ortho-vanadate (VO₄³⁻), and meta-vanadate (VO₃⁻) solutions and kept at room temperature for 5 min and 1 h with continuous stirring, respectively. Resulting precipitates were recovered by filtration, washed with water, and dried at 60 °C for a day.

3. Reaction time-dependent adsorption of tungstate anions on LYH:Tb

The aqueous solution (100 ppm) was prepared by dissolving Na₂WO₄·2H₂O in deionized

waters at room temperature. LYH:Tb powder (200 mg) was added to 20 mL of aqueous tungstate ($WO_4^{2^-}$) solution and kept at room temperature for 5 min, 10 min, 30 min, 1 h, 3 h, 6 h, and 12 h with continuous stirring. Resulting precipitates were recovered by filtration, washed with water, and dried at 60 °C for a day.

4. Concentration-dependent adsorption of tungstate anions on LYH:Tb

The aqueous stock solution (10000 ppm) were prepared by dissolving $Na_2WO_4 \cdot 2H_2O$ in deionized waters at room temperature. This solution was diluted to 1000, 100, 10, and 1 ppm. LYH:Tb powder (200 mg) was added to 20 mL of 1 – 10000 ppm aqueous solutions and kept at room temperature for 5 min with continuous stirring. Resulting precipitates were recovered by filtration, washed with water, and dried at 60 °C for a day. The amount of tungstate ion adsorbed on the surface of LYH:Tb was determined by ICP analysis of obtained powder.

5. Characterization

The chemical compositions were determined by inductively coupled plasma (ICP; Thermo Elemental Thermo ICAP 6000). Thermogravimetric (TG) curve was recorded in air at a heating rate of 5 °C/min using a Seiko Instruments TG/DTA320. The powder XRD patterns of LYH:Tb and its oxometalate adsorbed products were recorded with a Bruker D8 Advance diffractometer. The photoluminescence spectra were measured at room temperature using FP-6600 spectrophotometer (JASCO) with a Xenon flash lamp.



Fig. S1 TGA curve of as-synthesized $Y_{1.90}Tb_{0.10}(OH)_5NO_3 \cdot nH_2O$ (LYH:Tb). Considering the possible water adsorbed to the particle surface and the variable amount of interlayer water, the 7.78 % observed weight loss below 200 °C is close to the 7.52 % calculated losses from the dehydration of $Y_{1.90}Tb_{0.10}(OH)_5NO_3 \cdot 1.5H_2O$ to $Y_{1.90}Tb_{0.10}(OH)_5NO_3$.



Fig. S2 X-ray diffraction patterns of LYH:Tb powders (a) before and after reaction for 5 min in 10^2 ppm aqueous solutions of (b) CrO_4^{2-} , (c) MoO_4^{2-} , (d) VO_3^{-} , (e) VO_4^{3-} , and (f) WO_4^{2-} .



Fig. S3 The adsorption of WO_4^{2-} on the LYH:Tb after reaction in 10^2 ppm tungstate solution was confirmed by the energy dispersive X-ray spectroscopy.



Fig. S4 (a) Excitation ($\lambda_{em} = 544 \text{ nm}$) and (b) emission ($\lambda_{ex} = 266 \text{ nm}$) spectra of LYH:Tb powders after reaction for 1 h in 10⁴ ppm aqueous solutions of CrO₄²⁻, MoO₄²⁻, VO₃⁻, VO₄³⁻, and WO₄²⁻.



Fig. S5 X-ray diffraction patterns of LYH:Tb powders after reaction for 5 min in 10^2 ppm aqueous WO₄²⁻ solutions of pH = (a) 3.0, (b) 5.0, and (c) 7.0.



Fig. S6 (a) Excitation ($\lambda_{em} = 544 \text{ nm}$) and (b) emission ($\lambda_{ex} = 266 \text{ nm}$) spectra of LYH:Tb powders after reaction for 5 min in 10² ppm aqueous WO₄²⁻ solutions of pH = 3.0, 5.0, and 7.0.



Fig. S7 (a) Excitation ($\lambda_{em} = 544 \text{ nm}$) and (b) emission ($\lambda_{ex} = 266 \text{ nm}$) spectra of LYH:Tb powders after reaction for 5 min in 10⁴ ppm aqueous WO₄²⁻ solutions of pH = 2.5, 5.5, and 9.0. The wavelength of maximum excitation intensity shows a red shift ($266 \rightarrow 272 \text{ nm}$) with decreasing solution pH.



Fig. S8 X-ray diffraction patterns of LYH:Tb powders (a) before and after reaction for 5 min in (b) 1 ppm, (c) 10 ppm, (d) 10^2 ppm, (e) 10^3 ppm, and (f) 10^4 ppm aqueous WO₄²⁻ solutions.



Fig. S9 (a) Excitation ($\lambda_{em} = 544 \text{ nm}$) and (b) emission ($\lambda_{ex} = 266 \text{ nm}$) spectra of LYH:Tb powder (200 mg) after reaction for 5 min in 20 mL (red line) and 40 mL (blue line) of 10^2 ppm aqueous WO₄²⁻ solution.



Fig. S10 (a) Excitation ($\lambda_{em} = 544 \text{ nm}$) and (b) emission ($\lambda_{ex} = 266 \text{ nm}$) spectra of LYH:Tb powders, 200 mg (red line) and 400 mg (blue line), after reaction for 5 min in 20 mL of 10^2 ppm aqueous WO₄²⁻ solution.



Fig. S11 SEM images of LYH:Tb prepared (a) under hydrothermal condition and (b) as a slurry type at room temperature. The tungstate concentration dependent (c) excitation and (d) emission spectra of LYH:Tb with different size. Because the surface area depends on the crystalline size, the adsorption amount is strongly influenced by the crystalline size. Thus, the PL intensity of LYH:Tb with smaller size (i.e. larger surface area; slurry) was significantly enhanced when the tungstate concentration was increased from 10^2 to 10^4 ppm. In contrast, the same increase of tungstate concentration induced no significant difference in the PL intensity of LYH:Tb with larger size (i.e. smaller surface area; powder).



Fig. S12 (a) Excitation ($\lambda_{em} = 544$ nm) and (b) emission ($\lambda_{ex} = 254$ nm) spectra of $Y_{0.95}Tb_{0.05}(OH)_3$ (YH:Tb) powders recovered 3 h after addition into aqueous tungstate solutions as a function of tungstate concentration.