### **Electronic Supplementary Information**

# Inner filter effect of Cr(VI) on Tb-doped layered rare earth hydroxychlorides: New fluorescent adsorbents for the simple detection of Cr(VI)

Hyunsub Kim, Byung-Il Lee and Song-Ho Byeon\*

Department of Applied Chemistry, College of Applied Science, Kyung Hee University, Gyeonggi, 446-701, Korea

E-mail: shbyun@khu.ac.kr

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### **Experimental details**

## Synthesis of $RE_{2-x}Tb_x(OH)_5Cl \cdot mH_2O$ (RE = Pr, Nd, Sm, Eu, Gd, Dy, Er, and Y; 0.0020 $\leq x \leq 0.20$ )

Stoichiometric amounts of RECl<sub>3</sub>·6H<sub>2</sub>O and TbCl<sub>3</sub>·6H<sub>2</sub>O (10 mmol) were dissolved in deionized water (40 mL). The KOH (20 mmol) solution was then added drop-wise to the prepared mixture (OH<sup>-</sup> : RE<sup>3+</sup> ratio = 2 : 1) with vigorous stirring at room temperature. The resulting solution was aged at room temperature for 12 h. After the reaction was complete, the solid RE<sub>2-x</sub>Tb<sub>x</sub>(OH)<sub>5</sub>Cl·*m*H<sub>2</sub>O products were collected by several repeated filtrations (20,000 rpm, 10 min) and washings with distilled water and dried at 40 °C for 6 h.

### Adsorption Experiments

Cr(VI) stock solution (1.00 × 10<sup>2</sup> mM, 500 mL) was prepared by diluting ~10 mL of solution containing 7.3536 g of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) to 500 mL in a standard flask. The effect of pH was investigated by adjusting solution pH from 3.0 to 9.0 using 0.1 M HCl or 0.1 M NaOH under an initial Cr(VI) concentration of 10 mM, which was prepared by diluting the original stock solution. The proper amount of stock solutions was used in the preparation of calibration curves and the adsorption reaction procedures.

The LYH:*x*Tb (200 mg) sorbent was immersed into 50 mL of 10 mM Cr(VI) solutions (pH = 4.0 and 8.0) at room temperature with constant stirring (850 rpm). After adsorption reaction for 30 s – 72 h, the solution was recovered at specific time intervals using the syringe filter. The filtrates (1.0 mL) were diluted to 50.0 mL and adjusted to pH = 4.0 and 8.0, respectively. The Cr(VI) concentration of each solutions were determined by using the calibration curves prepared by UV-vis spectroscopic measurements.

The 1.0  $\mu$ M – 1.0 mM Cr(VI) solutions were prepared by serial dilution of stock solutions and the initial pH was adjusted to 4.0 and 8.0 using KOH and HCl solutions. A 200 mg of LRH:*x*Tb was introduced into 20 mL each solution of different Cr(VI) concentration with continuous stirring (850 rpm) for 5 min – 1 h. The solid product was isolated by filtration, washed with water, and then dried at 60 °C for 6 h. The obtained powder analyzed by measuring the excitation and emission spectra.

#### **Characterizations**

XRD patterns of  $RE_{2-x}Tb_x(OH)_5Cl \cdot mH_2O$  were recorded with a Bruker D8 Advance

diffractometer. Thermogravimetric (TG) analysis was performed in air at a heating rate of 5°C/min using a Seiko Instruments TG/DTA320. The absorption spectra were obtained on an Shimadzu Multispec-1501 and a LAMBDA 35 UV–vis spectrophotometer. The excitation and emission spectra were recorded on a FP-6600 spectrophotometer (JASCO) with a Xenon flash lamp. Field emission scanning electron microscopy (FE-SEM) was carried out with a Carl Zeiss LEO SUPRA 55 electron microscope operating at 30 kV. Specimens for the FE-SEM were coated with Pt-Rh for 180 s under vacuum.



**Fig. S1** UV-vis absorption spectra of 0.1 mM aqueous Cr(VI) solution as a function of solution pH.



**Fig. S2** Powder XRD patterns of  $RE_{1.90}Tb_{0.10}(OH)_5Cl \cdot nH_2O$  (LRH:5%Tb) slurries where RE = (a) Pr, (b) Nd, (c) Sm, (d) Eu, (e) Gd, (f) Dy, (g) Er, and (h) Y.



**Fig. S3** Emission spectra of  $RE_{1.90}Tb_{0.10}(OH)_5Cl \cdot nH_2O$  (LRH:0.1Tb) monitored at 254 nm excitation wavelength, where RE = (a) Gd and (b) Y.



**Fig. S4** (a) Excitation ( $\lambda_{em} = 545 \text{ nm}$ ) and emission spectra at  $\lambda_{ex} = (b) 254$  and (c) 379 nm of  $Y_{2.00-x}Tb_x(OH)_5 \cdot nH_2O$  (LYH:*x*Tb) as a function of Tb<sup>3+</sup> concentration (*x*).

**Table S1.** Solution pHs before and 10 min after immersing LYH:0.1Tb powder in the blank and 1.0  $\mu$ M, 0.1 mM, and 1.0 mM aqueous Cr(VI) solutions. The initial pHs were adjusted to 4.0 and 8.0 for all solutions.

Cr(VI)	Initial pH	Final pH
concentration		
0 -	4.0	7.4
	8.0	7.4
1.0 μM -	4.0	7.3
	8.0	7.4
0.1 mM -	4.0	7.3
	8.0	7.3
1.0 mM	4.0	7.3
	8.0	7.3



**Fig. S5** Effects of pH on the adsorption capacity of LYH:0.1Tb for Cr(VI) at an initial concentration of 10 mM. The  $q_t$  is the amount (mg/g) of Cr(VI) adsorbed on LYH:0.1Tb adsorbent at time t(min). The initial pHs were adjusted to 4.0 (blue curve) and 8.0 (red curve).



**Fig. S6** Comparison of XRD pattern for LYH:0.1Tb (a) before and after reaction in 10 mM aqueous Cr(VI) solution at the initial pH = (b) 4.0 and (c) 8.0 for 72 h at room temperature.



**Fig. S7** SEM images of LYH:0.1Tb (a) before and after adsorption reaction in 1.0 mM aqueous Cr(VI) solutions at the initial pH = (b) 4 and (c) 8, respectively (bar = 100 nm).



**Fig. S8** Emission spectra of LGdH:0.1Tb recovered 10 min after reaction in 1.0  $\mu$ M, 0.1 mM, and 1.0 mM aqueous Cr(VI) solutions at initial pHs = (a) 4.0 and (b) 8.0.



**Fig. S9** Relative intensities of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  emission at 545 nm of LYH:0.1Tb recovered after reactions in (a) 1.0 mM, (b) 0.1 mM, and (c) 1.0  $\mu$ M aqueous Cr(VI) solutions at the initial pH = 4.0 (blue lines) and 8.0 (red lines) for 5, 10, 30 and 60 min.



**Fig. S10** Relative intensities of  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  emission at 545 nm of LYH:0.1Tb recovered 10 min after reactions in 1.0  $\mu$ M, 0.1 mM, and 1.0 mM aqueous Cr(VI) only solutions (blue) and aqueous solutions (red) containing all of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup> (or PO<sub>4</sub><sup>3-</sup>), and CO<sub>3</sub><sup>2-</sup> anions at the initial pH = (a) 4.0 and (b) 8.0.