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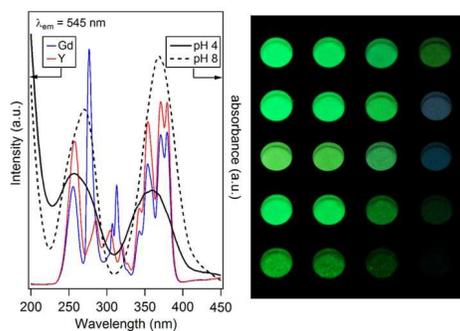
Graphical Abstract

"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*

The effective overlap of excitation bands of Tb-doped layered yttrium hydroxychlorides with absorption bands of Cr(VI) (both $HCrO_4^-$ and CrO_4^{2-} forms) constructs a new inner filter effect system resulting in fluorescence quenching.

ARTICLE TYPE

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*

Terbium-doped layered yttrium hydroxychlorides (LYH:xTb) were explored for the simple and convenient detection of Cr(VI) in aqueous solution, where the effective overlap of
10 **excitation bands of LYH:xTb with absorption bands of Cr(VI) constructs a new inner filter effect system. The shielding of excitation light for LYH:xTb by adsorbed Cr(VI) was so effective that a feasible detection sensitivity could be achieved.**

Layered rare earth hydroxides (LRHs) of the general formula
15 $RE_2(OH)_5X \cdot nH_2O$ (RE = rare earths, X = interlayer anions), composed of alternately stacked $[RE_2(OH)_5 \cdot nH_2O]^+$ rare earth hydroxocation layers and X^- anion layers, are an emerging class of materials with a wide range of potential applications.[1] Compared to classical layered double hydroxide (LDHs), LRHs
20 have several advantages such as simple preparation, environmentally sensitive and efficient optical properties, and tunable excitation and emission spectra. To date, this family of layered materials has been investigated as catalysts,[2] precursors for luminescent films,[3] and contrast agents for magnetic
25 resonance (MR) imaging and probe materials.[4] In particular, because the great number of hydroxyl groups at their surface can form a hydrogen bonding network, LRH nanosheets are well dispersed in polar solvents,[5] and therefore, they have been examined to detect and separate thiols in aqueous solution.[6]
30 Recently, we demonstrated that the antenna effect and selective excitation energy transfer to the LRH matrix can be employed to simply detect and remove trace amounts of tungstate ions from an aqueous solution.[7] Thus, the adsorption ability and selectivity of LRHs are promising for the detection and removal of heavy
35 metal-oxoanions. In the present work to further understand the effect of oxoanion adsorption on the optical behavior of LRHs, we found that the adsorption of chromates induced effective quenching of the emission of some Tb-doped layered rare earth hydroxychlorides (LRH:Tb) due to the inner filter effect (IFE) of
40 Cr(VI) (both $HCrO_4^-$ and CrO_4^{2-} forms).

Hexavalent chromium Cr(VI) is regarded as hazardous due to its mutagenicity and carcinogenicity to living organisms, and its facile solubility in neutral water allows it both mobility and bio-accessibility.[8] Because the maximum allowed limit of Cr(VI) is
45 strictly regulated for many water sources around the world,[9] simple and fast detection methods are necessary to monitor and maintain Cr(VI) concentrations in environmental waters at lower than limited levels. Among many separation techniques, such as chemical precipitation, solvent extraction, membrane
50 nanofiltration, reverse osmosis, ion exchange, and electrodialysis,[10] adsorption has recently been considered one of the most promising methods.[11] For selection of an adsorption method to detect and remove Cr(VI), extensive investigations have been carried out to improve traditional adsorbents such as
55 activated carbon, titanium dioxide, silica gel, zeolites, and clay, or to develop alternative adsorbents, which are more efficient and cost effective.[12]

The IFE, one of non-irradiation energy conversions, stems from absorption of excitation and/or emission light for
60 fluorescent adsorbents by adsorbates.[13] Thus, the spectral overlap of the adsorbate absorption band with the adsorbent excitation and/or emission band is a crucial factor in determining the efficiency of the IFE. Because no covalent interactions between the energy receptor and donor are required, the IFE has been
65 employed in the design and development of novel probes for highly sensitive fluorescent assays.[14] Yet, it is challenging to develop a new IFE system for the sensitive fluorescent detection of Cr(VI). Here, we demonstrate a Tb-doped layered yttrium hydroxychloride (LYH:Tb) sensor as a representative example of
70 LRH adsorbents for the detection of Cr(VI) based on the IFE. The effective shielding of excitation light for LYH:Tb by adsorbed Cr(VI) could achieve a feasible IFE-based detection sensitivity. This LYH:Tb detector provides a simple, convenient, rapid, and sensitive method for the detection of Cr(VI), which has potential
75 environmental applications. The striking contrast in brightness of green emission before and after adsorption of Cr(VI), which is distinguishable even with the naked eye, would enable LYH:Tb powder to be exploited as a portable kit for field detection of Cr(VI) in environmental and industrial waste waters.

80 In dilute aqueous solution, Cr(VI) exists as the hydrochromate ($HCrO_4^-$) and chromate (CrO_4^{2-}) forms, whose relative ratio depends on the solution pH.[15] According to the chemical equilibrium, $HCrO_4^- + OH^- \leftrightarrows CrO_4^{2-} + H_2O$, $HCrO_4^-$ is predominant at lower pH whereas the concentration of the
85 deprotonated CrO_4^{2-} form increases at higher pH. When the UV-vis spectrum of aqueous Cr(VI) solution was measured as a function of pH (Fig. S1, ESI†), gradual changes in both position and intensity of absorption bands were observed with increasing solution pH up to ~ 7, while no significant difference was

observed at pHs higher than 7. This observation is consistent with a previous report that only CrO_4^{2-} is stable at pH > 6.8.[16] Nevertheless, two distinct absorption bands were consistently observed in the experimental pH range regardless of the dominant species ($HCrO_4^-$ and/or CrO_4^{2-}).

$RE_{2.0-x}Tb_x(OH)_5Cl \cdot nH_2O$ (LRH:xTb, RE = Pr, Nd, Sm, Eu, Gd, Dy, Er, and Y; x = 0.20, 0.10, 0.020, and 0.0020) were prepared using aqueous solutions of $RECl_3 \cdot 6H_2O$ and $TbCl_3 \cdot 6H_2O$ at room temperature (see Experimental, ESI†). Systematic (00l) reflections observed in the powder X-ray diffraction (XRD) patterns of the products confirmed the formation of a typical layered structure with gallery heights of 8.6 – 8.7 Å depending on the nature of the RE (Fig. S2, ESI†). The interlayer water content (n) was determined to be 1.0 – 2.0 by thermogravimetric (TG) analysis.

Excitation and emission spectra of LRH:xTb were measured to investigate the extent of spectral overlap with the absorption bands of Cr(VI), which is required for high efficiency of the IFE. As shown in Fig. 1a, when RE = Gd and Y, the excitation spectra of LRH:0.1Tb had several strong bands originating from $4f^8 \rightarrow 4f^75d^1$ and intra-$4f^8$ transitions in the 200 – 400 nm UV region. By contrast, no discernible band was observed with other RE members (Fig. 1a, inset), indicating the UV absorption energy level different from the resonance level of Tb^{3+} in these matrix. The emission spectra of RE = Gd and Y members under excitation at 254 nm showed typical $^5D_4 \rightarrow {}^7F_J$ bands of Tb^{3+} (Fig. S3, ESI†). It is of interest that the broad absorption bands of Cr(VI) at approximately 260 and 360 nm, irrespective of pH, overlapped quite well with the excitation bands of LRH:0.1Tb (RE = Gd and Y) as compared in Fig. 1b. Thus, the adsorptions of Cr(VI) were expected to efficiently shield the excitation light for LRH:0.1Tb (RE = Gd and Y) such that a new IFE system would be constructed resulting in fluorescence quenching. Therefore, we examined in depth $Y_{2.0-x}Tb_x(OH)_5Cl \cdot nH_2O$ (LYH:xTb) as a

Fig. 1 (a) Excitation spectra (λ_{em} = 545 nm) of LRH:0.1Tb (RE = Pr, Sm, Nd, Eu, Gd, Er, Dy, and Y). The band observed at shorter than 260 nm corresponds to the $4f^8 \rightarrow 4f^75d^1$ transition and several bands at 270 – 400 nm are attributed to intra-$4f^8$ transitions of Tb^{3+} ions; $^7F_6 \rightarrow {}^5F_{5,4}$ (~ 280 nm), $^5H_{7-4}$ (~ 300 nm), $^5D_{1,0}$ (~ 315 nm), $^5L_{10-7}$ (~ 345 nm), $^5G_{6-2}$ (~360 nm), and $^5D_{2-4}$ (~ 375 nm). Inset: Enlarged spectra in the 220 – 410 nm wavelength region show excitations of RE = Pr, Sm, Nd, Eu, Er, and Dy members. (b) Comparison of excitation spectra of LRH:0.1Tb (RE = Gd and Y) and UV-vis absorption spectra of 0.1 mM aqueous Cr(VI) solutions at pH = 4.0 (black solid curve) and 8.0 (black dotted curve).

representative example to ensure that the IFE of Cr(VI) takes place in a sensitive manner.

The excitation and emission spectra of LYH:xTb showed a systematic dependence on the activator concentration (x). In particular, it was noted that the change in intensity was most distinctive for excitation at ~379 nm ascribed to the $^7F_6 \rightarrow {}^5D_3$ transition of Tb^{3+} (Fig. S4, ESI†). In this paper, we describe the behavior of fluorescence quenching by the IFE of Cr(VI) on the x = 0.10 member (LYH:0.1Tb), as an example. To assess the effect of LYH:0.1Tb on solution pH, the variation of pH was monitored before and 10 min after immersing LYH:0.1Tb powder in blank and Cr(VI) solutions of different concentrations (Table S1, ESI†). Although the initial pHs were differently adjusted to 4.0 and 8.0, the pHs after 10 min were quite similar (7.3 – 7.4) to each other at every concentrations, and the equilibrium pH was slightly lowered with increasing Cr(VI) concentration. Furthermore, when adsorption reactions of LYH:0.1Tb were performed in 10 mM aqueous Cr(VI) solutions at an initial pH = 4.0 or 8.0, the measured maximum adsorption amounts of Cr(VI) were not very different from each other regardless of the initial pH. As shown in Fig. S5 (ESI†), the adsorbed amount of Cr(VI) on LYH:0.1Tb increased with contact time reaching a plateau after approximately 1 h, indicating that the adsorption reaction was essentially complete. Based on the calibration curve for Cr(VI) concentration in aqueous solution, the adsorption capacity (~80 mg/g) of LYH:0.1Tb for Cr(VI) at an initial pH = 8.0 was not significantly different in comparison with the capacity (~98 mg/g) at an initial pH = 4.0. This observation indicates that the surface of the hydroxide adsorbent is protonated at low pH (LYH:0.1Tb-OH + H_3O^+ → LYH:0.1Tb-OH_2^+ + H_2O), while deprotonation (LYH:0.1Tb-OH + OH^- → LYH:0.1Tb-O^- + H_2O) takes place at high pHs. Thus, LYH:xTb adsorbents are capable of buffering aqueous solutions to maintain similar adsorption capacity for Cr(VI) despite vastly different initial pHs. As the 10 mM concentration corresponds to a large excess of the exchange capacity of LYH:0.1Tb, no difference in its XRD pattern before and after the adsorption reaction with Cr(VI) for 72 h led us to believe that chromates essentially do not enter the interlayer gallery of LYH:0.1Tb to exchange with the original Cl^- anions at least within 72 h at room temperature (Fig. S6, ESI†). Scanning electron microscopy (SEM) images of LYH:0.1Tb showed well-developed sheet-like morphology (Fig. S7, ESI†). No difference in lateral dimension (50–200 nm) and surface morphology before and after adsorption reaction was consistent with the maintenance in XRD pattern.

By contrast, negatively charged species could be readily adsorbed by electrostatic interactions on the surface of positively charged LRH nanosheets, which was confirmed by zeta potential measurement.[17] Practically, LYH:xTb exhibited special adsorption and exchange characteristics with $HCrO_4^-$ and CrO_4^{2-} at the surface, and the concomitant IFE resulted in fluorescence quenching of LYH:xTb after reaction in aqueous Cr(VI) solutions. This observation suggested that the present IFE system could be an alternative approach for fluorescence detection of Cr(VI). To evaluate the sensitivity for $HCrO_4^-$ and CrO_4^{2-} detection, LYH:0.1Tb was dispersed in aqueous Cr(VI) solutions of different concentrations at initial pH = 4.0 and 8.0. Fig. 2 displays the typical emission spectra of LYH:0.1Tb recovered after
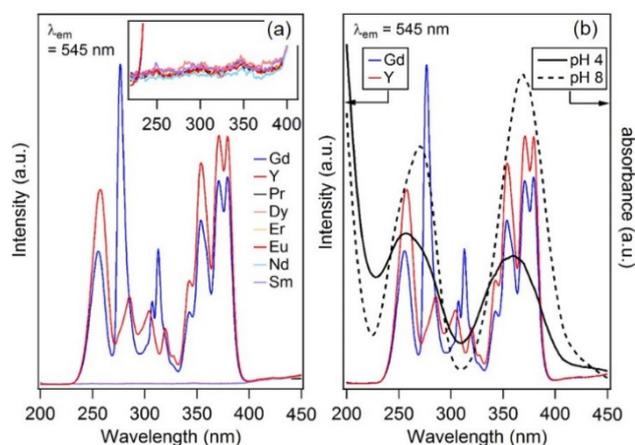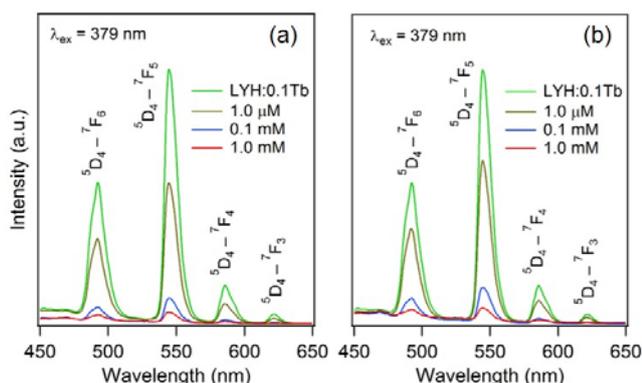
Fig. 2 Emission spectra of LYH:0.1Tb recovered 10 min after reaction in 1.0 μM, 0.1 mM, and 1.0 mM aqueous Cr(VI) solutions at initial pHs = (a) 4.0 and (b) 8.0.

Fig. 4 Photographs of LYH:*x*Tb under 254 nm UV irradiation as a function of doping concentration (*x*). LYH:*x*Tb was recovered after reaction in (a) 1.0 μM, (b) 5.0 μM, (c) 0.1 mM, and (d) 1.0 mM aqueous Cr(VI) solution for 10 min at the initial pH = 4.0 and 8.0. Photographs of LYH:*x*Tb in aluminum holders were taken to illustrate the potential for a portable kit.

reactions for 10 min as a function of Cr(VI) concentration (from 1.0 μM to 1.0 mM). When measured at 379 nm excitation, the strong emission intensity of LYH:0.1Tb was greatly reduced with increasing concentrations of Cr(VI). Essentially the same

5 behaviour was also observed with LGdH:0.1Tb in the same experimental conditions (Fig. S8, ESI†). Considering the good spectral overlap between the absorption bands of Cr(VI) and the excitation bands of LYH:0.1Tb (Fig. 1b), such a decrease in emission intensity is attributed to the shielding of excitation light

10 for LYH:0.1Tb by adsorbed $HCrO_4^-$ and/or CrO_4^{2-}. For the same reaction times, the initial pH (pH = 4.0 or 8.0) had no significant influence on the extent of fluorescence quenching (Fig. S9, ESI†), because the equilibrium pHs were similar. In particular, it was noted that a fluorescence quenching of 30 – 40 % was induced

15 within 10 min by the adsorption reaction in 1.0 μM (52.0 μg/L) Cr(VI) solution. As the maximum contaminant level of Cr(VI) in domestic water supplies is regulated to lower than 50 μg/L,[9] the IFE of our system would enable LYH:0.1Tb adsorbent to simply monitor Cr(VI) the concentration in drinking water.

20 The effect of common anions on the fluorescence quenching of LYH:0.1Tb was examined by measuring the emission intensity of $^5D_4 \rightarrow {}^7F_5$ transition after reaction in pure water and aqueous solutions containing Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} (or PO_4^{3-}), and CO_3^{2-} at three different concentrations (1.0 μM, 0.1 mM, and 1.0

25 mM). As shown in Fig. 3, compared with distinct concentration dependent decrease in emission intensity by $HCrO_4^-$/CrO_4^{2-}, other tested anions had no significant influence on the fluorescence of LYH:0.1Tb at both initial pH = 4.0 and 8.0 within at least 10 min. Although NO_3^- and SO_4^{2-} anions induced a little

30 decrease in relative emission intensity at high concentration level, their fluorescence change was not comparable with those by Cr(VI). The fluorescence quenching of LYH:0.1Tb by Cr(VI) adsorption was also reproduced similar even in the simultaneous presence of these five anions (Fig. S10, ESI†).

35 Moreover, if we appropriately select the doping concentration (*x*) of Tb^{3+}, the degree of fluorescence quenching of LYH:*x*Tb is even visually distinguishable, depending on the adsorbed amount of Cr(VI). As shown in Fig. 4, after adsorption of Cr(VI) on LYH:*x*Tb at initial pH = 4.0 and 8.0, significant darkening under

40 a commercially available 254 nm UV lamp was observed with the naked eye. A lower doping amount (*x*) of Tb^{3+} is desirable for the detection of lower Cr(VI) concentrations, because a visually distinguishable difference in brightness can be achieved before and after adsorption. For instance, when we used an *x* = 0.002

45 adsorbent, visual detection simply from the change in brightness was successful down to 5.0 μM Cr(VI) contamination irrespective of the solution pH (Fig. 4b). By contrast, when LYH:0.2Tb (*i.e.*

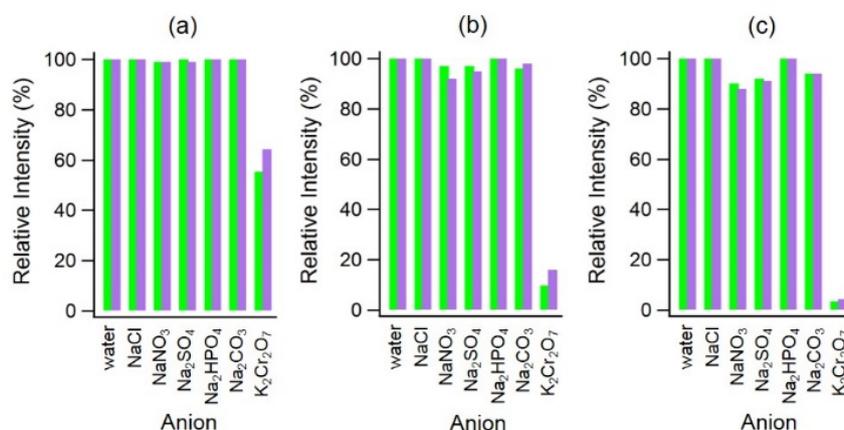**Fig. 3** Relative intensities of $^5D_4 \rightarrow {}^7F_5$ emission at 545 nm of LYH:0.1Tb recovered 10 min after reactions in pure water and (a)1.0 μM, (b) 0.1 mM, and (c) 1.0 mM aqueous solutions of NaCl, NaNO₃, Na₂SO₄, Na₂HPO₄, and Na₂CO₃ at the initial pH = 4.0 (green) and 8.0 (violet).
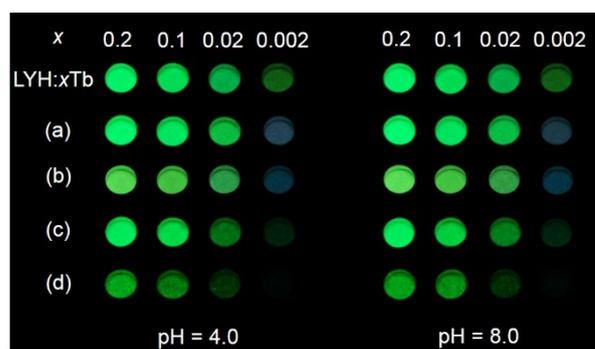
high Tb^{3+} doping concentration) was used, the degree of darkening after reaction even in 0.1 mM Cr(VI) solution was too weak to be distinguishable from the strong brightness before adsorption (Fig. 4c). Therefore, this simple and convenient IFE system could also be applied as a portable detection kit to collect and instantly ascertain the presence or approximate contamination level of Cr(VI) in the field.

In conclusion, we have demonstrated that an inner filter effect system is constructed by the effective overlap between the excitation bands of LYH:xTb and absorption bands of Cr(VI) (both $HCrO_4^-$ and CrO_4^{2-} forms). This IFE system enables LYH:xTb adsorbents to be potentially applicable as a new fluorescent detector for Cr(VI) in aqueous solution. Besides simplicity and convenience, the buffering capability of LYH:xTb provides the advantage of significant fluorescence quenching in both acidic and basic solutions at room temperature. Therefore, it should be possible to use our system for monitoring chromium contamination at low concentration levels in natural surface water bodies or wastewater treatment plants. We are further investigating related LRH materials to exploit their anion-adsorbing properties with other harmful metal-oxoanions.

Notes and references

Department of Applied Chemistry, College of Applied Science and Institute of Natural Sciences, Kyung Hee University, Gyeonggi 446-701, Korea. Fax: +82-31-201-2340; Tel: +82-31-201-2457; E-mail: shbyun@khu.ac.kr

† Electronic Supplementary Information (ESI) available: Experimental details, Additional powder XRD patterns, UV-vis spectra and excitation and emission spectra, Table of initial and final pHs, Graph of adsorption capacity and relative emission intensity as a function of adsorption reaction time, Graph showing the effect of common anions on the fluorescence quenching of LYH:Tb. See DOI: 10.1039/b000000x/

‡ These authors equally contributed to this work.

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