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Synthesis of Eu^{3+}-Doped Layered Double Hydroxide with Nitrate Detection Ability

Nitrate anion species is known to have a significant impact on the aquatic environment and living organism. Therefore, the wastewater standard and amount of these toxic species released into water is limited by law and set by worldwide. So, there is a need to accurately detect the presence of these toxic anion species in water on site and develop materials that can effectively remove them from water. Recently, we found that the photoluminescence (PL) intensity of Tb^{3+}-doped layered double hydroxide (LDH) consisting of Mg and Al varies depending on the anion species incorporated into interlayer space.[1] In this study, we synthesized the Eu^{3+}-doped LDH consisting of Mg and Al (Eu-LDH) with chloride anions as exchangeable anion and then investigated its nitrate selectivity and detection performance by photoluminescence changes.

Eu-LDH with carbonate anion was synthesized by hydrothermally treating the mixed aqueous solution ([Mg^{2+}]: [Al^{3+}] : [Eu^{3+}] : [hexamethylenetetramine] = 100 mmol/L : 48.5 mmol/L : 1.5 mmol/L : [175 mmol/L] at 140℃ for 24 h with reference to literature.[2] Eu-LDH with chloride anions as starting materials for anion-exchange experiment from chloride to nitrate was prepared by HCl-EtOH decarbonate method.[3] Anion-exchange experiments were carried out by dispersing Eu-LDH with chloride anion to NaCl-$NaNO_3$ mixed solutions with various mixing ratio.

In Figs. 1-A and B, XRD patterns and FT-IR spectra of Eu-LDHs with carbonate and chloride anions are shown. It was found that the target Eu-LDHs with carbonate and chloride anions were successfully synthesized. PL spectra of Eu-LDHs obtained after anion-exchange from chloride to nitrate anions showed PL quenching depending on the initial nitrate concentration. On the other hand, no significant change in the shape of the PL spectra could not be observed. The $I(^5D_0\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_1)$ values linearly

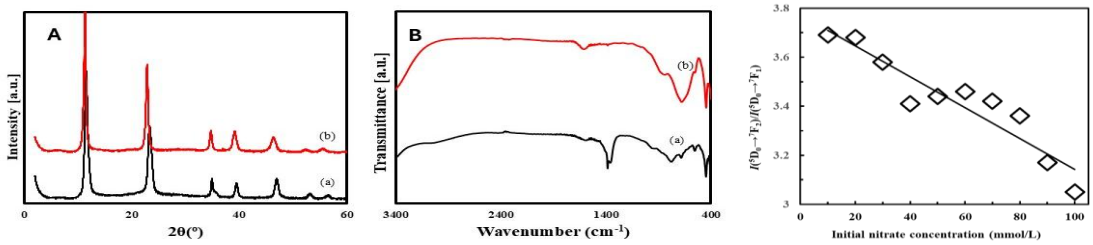

Fig. 1. (A) XRD patterns, (B) FT-IR spectra of Mg (Al, Eu)LDHs with carbonate (a) and chloride (b) anions. (C)Dependence of $I(^5D_0\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_1)$ of Eu-LDHs on initial nitrate concentration after anion exchange experiments.

decreased with an increase in the initial nitrate concentration. Therefore, this result indicates that the Eu-LDH is a material that can not only detect nitrate ions, but also selectively remove nitrate anion.

1. Sasai, R. *International Conference on Functional Layered Nanomaterials 2023* **2023**@Shimane University.
2. Chen, Y.; et al., *J. Solid State Chem.* **2010**, *183*, 2222.
3. Iyi, N.; et al., *Appl. Clay Sci.* **2011**, *54*, 13.