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Inorganic–Organic Hybrid Nonwoven Fabrics with Colorimetric Detection Capability for Borate Ions in Aqueous Solutions

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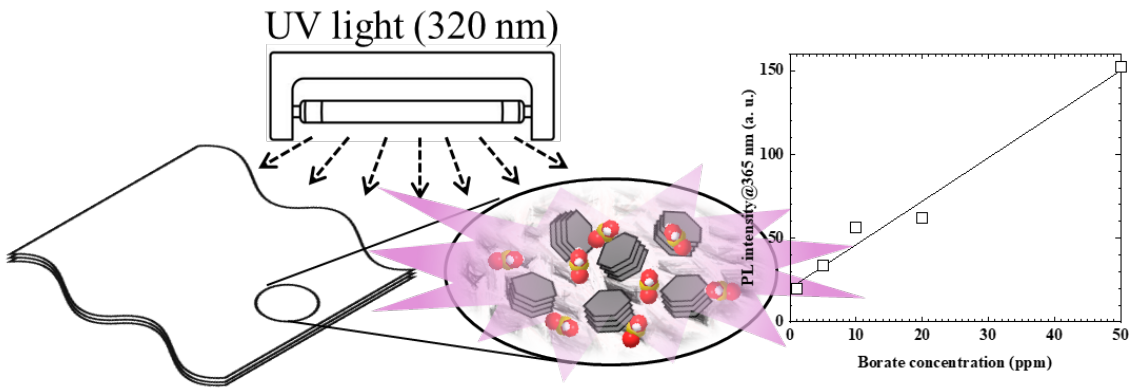
Abstract

A nonwoven fabric sheet with an immobilized colorimetric reagent was prepared to detect borate anions in aqueous media. The fabric comprised immobilized chromotropate and 1-butanesulfonate anions and chromotropate anions, as the colorimetric reagent, per anion-exchange capacity of the layered double hydroxide. The resulting sheet quantitatively detected borate anions through photoluminescence measurements. Thus, it can be used for onsite quantitative analysis of dissolved boron in water, with promising potential for water quality monitoring and consequently, sustainable and safe water resources globally.

Keywords: borate detection, layered double hydroxide, onsite quantitative analysis

Graphical abstract



Dissolved boron in water adversely affects plant growth and animal reproductive functions. To ensure the safety of water, particularly environmental water, a global water quality standard of 1 mg B/L has been established. Additionally, Japan has set effluent standards for controlling the release of boron into environmental water (10 and 230 mg B/L for nonmarine and marine areas, respectively).

Colorimetric or fluorometric analysis using chelating dyes is a well-known method for determining dissolved boron.[1–7] However, this method involves complicated procedures, such as appropriate pretreatment of sampled water, precise addition of a chelating dye, and maintaining rigorous conditions for sample-solution preparation. Consequently, colorimetric or fluorometric analysis is difficult to apply for rapid and simple onsite quantification. Meanwhile, test papers are promising materials for onsite detection. Nevertheless, their quantitative performance is low because their application is based on comparison with color charts. Hence, water samples need to be collected and quantified in laboratories. To this end, there is a high demand for materials that enable the rapid onsite determination of boron and devices that use such materials. One approach to meet these requirements is to solidify chelating dyes by hybridizing them with an inorganic host material.

Layered double hydroxides (LDHs), a type of anion-exchangeable layered inorganic compound, are well-known host materials. Several researchers have investigated hybrid materials comprising various functional organic compounds, such as dyes combined with LDHs.[8–14] Additionally, extensive research has been conducted on the preparation, characterization, and application of materials that can detect various molecules and/or ions, as summarized in the review by

Okada et al.[15,16] Our previous research encompassed the synthesis and characterization of hybrid materials formed by integrating layered inorganic compounds, such as smectite, LDHs, and α-zirconium phosphate, with various functional dyes that can detect specific molecules and ion species.[17–28] Date and colleagues[29] reported that a hybrid powder of LDH, *n*-butanesulfonate (C_4S), and chromotropate (CT) anions, reportedly used as a colorimeter for borate anions in aqueous solutions, can qualitatively determine borate anions on the basis of changes in luminescence. However, despite the detection ability of such hybrid powders, their application in the development of devices for rapid onsite quantitative measurements is challenging. When a hybrid powder is used, the concentration of borate anions must be determined by measuring the luminescence intensity of the powder. This is done by dispersing the powder in an environmental sample for a certain time, followed by solid–liquid separation through filtration and drying. This is a complicated process and difficult to conduct onsite, as in existing colorimetric and colorimetric fluorescence analysis. Yoshida et al.[29] proposed a hybrid material carrier method. They reported that a quantitative onsite luminescence-analysis device for borate anions in aqueous solutions could be realized if a membrane material could be developed for fixing the composite material.

In this study, chromotropic acid anions were immobilized as a colorimetric reagent on a LDH-loaded nonwoven fabric sheet to develop a membrane that can quantitatively detect boric-acid anions dissolved in an aqueous solution. The anions were detected through changes in the luminescence intensity. Moreover, the detection capability of this hybrid nonwoven fabric for borate anion species was quantified.

LDH-loaded nonwoven fabric sheets (hereafter "LDH-sheets") were provided by Nippon Shokubai Co., Ltd. The details of the preparation method are provided in the Supplementary Material. The LDH-sheet was immersed in an acetate–ethanol mixed solution (300% AEC: three times the amount of acetic acid as the anion-exchange capacity) and reacted at 40 °C for 24 h in a nitrogen atmosphere. Subsequently, it was washed several times with ethanol. After drying under reduced pressure, a nonwoven fabric sheet loaded with LDH and acetate anions as the interlayer anion species (Ac-LDH-sheet) was prepared. The Ac-LDH-sheet was immersed in decarbonated water containing sodium chromotropate (CT: x = 0.1%, 0.5%, and 1.0% AEC) and sodium butanesulfonate (C_4S: 200% AEC) and reacted at 25 °C for 24 h in a nitrogen atmosphere. After washing with ethanol and vacuum drying, a hybrid LDH-sheet containing CT and C_4S (denoted as CT(x)C_4S-LDH-sheet) was prepared. The as-prepared CT(x)C_4S-LDH-sheet was characterized via X-ray diffraction (XRD; MiniFlex II, RIGAKU, Japan) using Ni-filtered Cu Kα irradiation at 30 kV and 15 mA; diffuse reflectance (DR) spectroscopy (FP-6600, JASCO, Japan) in synchronous mode; and photoluminescence (PL) spectroscopy (FP-6600, JASCO, Japan) at an excitation wavelength of 320 nm.

Borate detection experiments using the CT(x)C_4S-LDH-sheet were conducted as per the following procedure. (1) A CT(x)C_4S-LDH-sheet (3 cm × 3 cm) was immersed in a sodium tetraborate solution (0.0, 1.0, 5.0, 10.0, 20.0, 50.0, and 100 ppm) for a specified duration (0–24 h). (2) The sheet was removed from the solution and dried under a stream of dry nitrogen gas. (3) The dried CT(x)C_4S-LDH-sheet was sandwiched between two quartz glass slides, and its PL spectrum was recorded using DR spectroscopy. Processes (1)–(3) were repeated for each sample.

The XRD patterns of all sheet samples are presented in Figure 1. Compared with those of LDH- and Ac-LDH-sheets, the XRD patterns of CT(x)C_4S-LDH-sheets contain two new diffraction peaks at 5.7° and 11.4°, whereas the diffraction peaks of Ac-LDH completely disappear. The 2θ values of these peaks matched those of the LDH powder combined with C_4S and fluorescein dyes, as previously reported,[21] indicating the incorporation of C_4S in the interlayer space of LDH in CT(x)C_4S-LDH-sheet, regardless of the x value (0.1, 0.5, and 1.0).

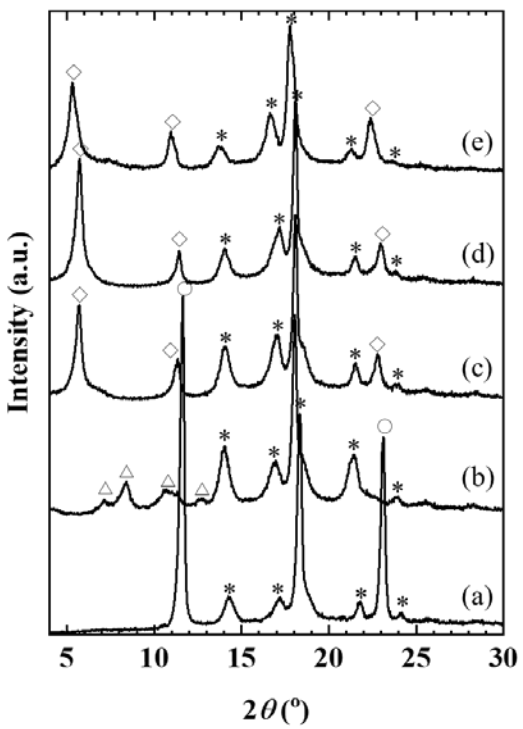


Fig. 1. XRD patterns of (a) LDH-sheet, (b) Ac-LDH-sheet, (c) CT(0.1)C_4S-LDH-sheet, (d) CT(0.5)C_4S-LDH-sheet, and (e) CT(1.0)C_4S-LDH-sheet. The symbols *, △, and ◇ represent the nonwoven fabric sheet, Ac-LDH, and CT(x)C_4S-LDH, respectively.

An adsorption band attributed to CT is observed in the DR spectra of the CT(x)C_4S-LDH-sheet (Figure 2). These

results confirm the preparation of the CT(*x*)C_4S-LDH-sheet. The bands corresponding to CT are not detected in the absorption spectra of the immersing solution after preparing CT(*x*)C_4S-LDH-sheet. This indicates that almost the entire amount of the added CT was incorporated into the interlayer space of the LDH in the nonwoven fabric sheet.

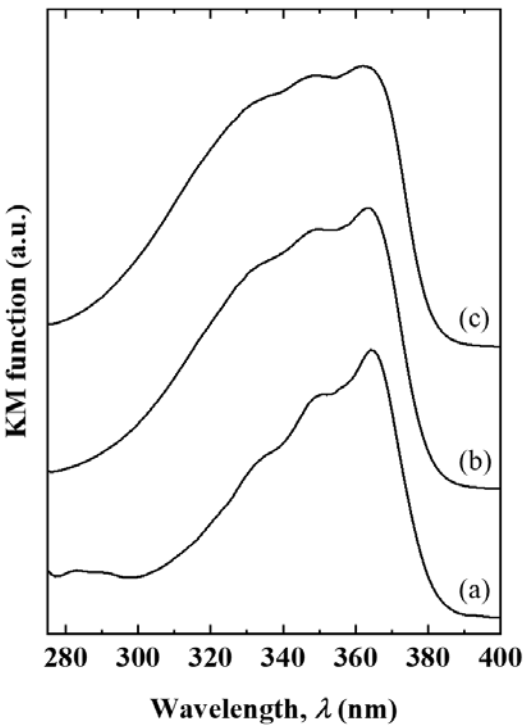


Fig. 2. DR spectra of (a) CT(0.1)C_4S-LDH-sheet, (b) CT(0.5)C_4S-LDH-sheet, and (c) CT(1.0)C_4S-LDH-sheet.

Figure 3 illustrates the PL spectra of CT(*x*)C_4S-LDH-sheets immersed momentarily (broken lines) and for 50 min (solid lines) in a 100-ppm aqueous sodium tetraborate solution. In the PL spectra of CT(*x*)C_4S-LDH-sheet immersed for 50 min, a new PL band is observed at approximately 365 nm regardless of the amount of CT incorporated. Moreover, in the PL spectra of CT(0.1)C_4S-LDH-sheet and CT(0.5)C_4S-LDH-sheet, a new PL band appears at approximately 385 nm. The new PL bands at approximately 365 and 385 nm are attributed to the complex formation between CT and borate anions.[30] These results indicate the enhanced PL of CT(*x*)C_4S-LDH-sheet in the presence of borate anions. Particularly, CT(0.1)C_4S-LDH-sheet has the most remarkable PL enhancement, suggesting its high sensitivity to borate anions.

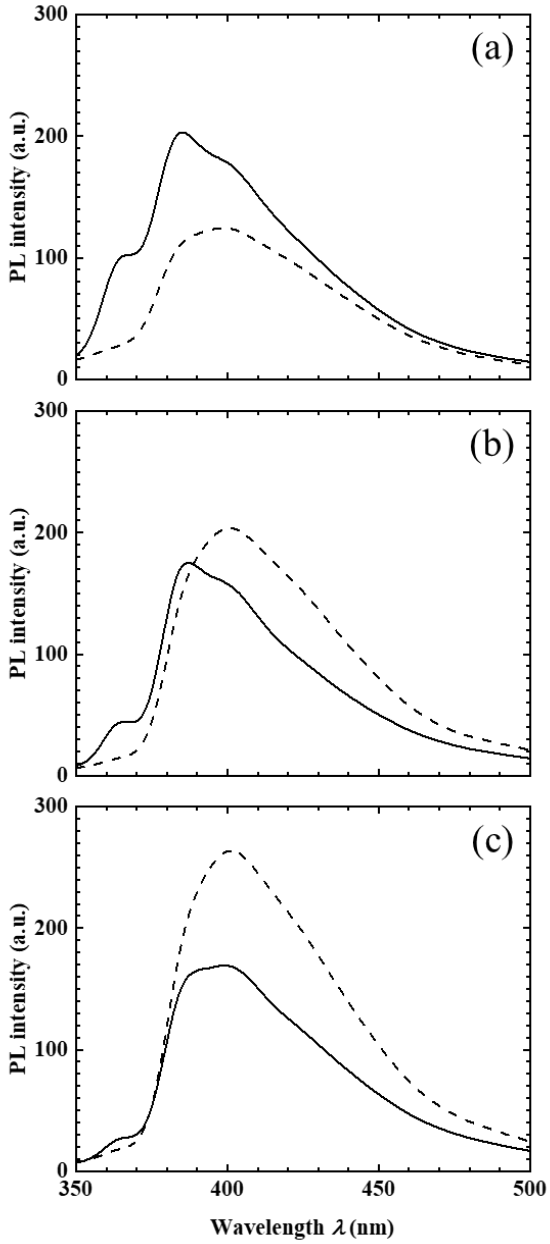


Fig. 3. PL spectra of (a) CT(0.1)C_4S-LDH-sheet, (b) CT(0.5)C_4S-LDH-sheet, and (c) CT(1.0)C_4S-LDH-sheet. Immersion time: momentary (broken lines) and 50 min (solid lines).

Figure 4 presents the PL intensity of CT(0.1)C_4S-LDH-sheet at 365 nm against the immersion time. The PL intensity at 365 nm increases with increasing immersion time up to approximately 30 min and then becomes almost constant for more than 30 min. This indicates the complete adsorption of borate anions onto CT(0.1)C_4S-LDH-sheet after immersion of 30 min.

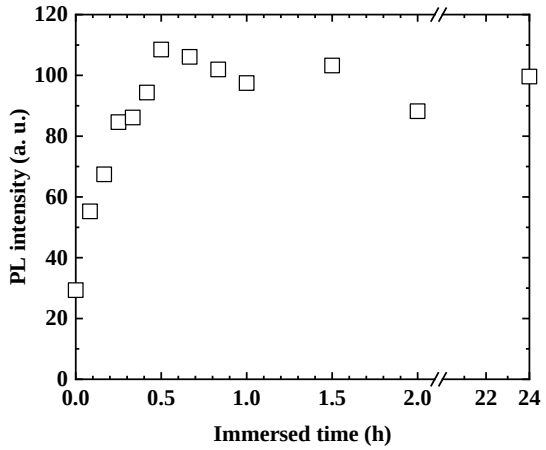


Fig. 4. Immersion-time dependence of PL intensity at 365 nm for CT(0.1)C_4S-LDH-sheet.

Figure 5 displays the PL spectra of CT(x)C_4S-LDH-sheet immersed in various concentrations of an aqueous sodium tetraborate solution for 50 min. The PL intensity increases with the borate concentration up to 50 ppm. However, when CT(x)C_4S-LDH-sheet was immersed in the 100-ppm aqueous sodium tetraborate solution, the PL intensity drastically decreases. The absorption band of a CT–borate complex is observed in the UV-Vis absorption spectrum of the aqueous solution obtained after immersing the sheet in the aqueous sodium tetraborate solution (100 ppm) for 50 min. This is because CT was partly extracted from CT(0.1)C_4S-LDH-sheet during immersion. The inset in Figure 5 presents the PL intensities at 365 nm as a function of borate concentration. The PL intensity at 365 nm increases linearly with increasing borate concentration up to 50 ppm (R^2 = 0.973). This result indicates that CT(0.1)C_4S-LDH-sheet can quantitatively detect borate at concentrations below 50 ppm based on the PL intensity.

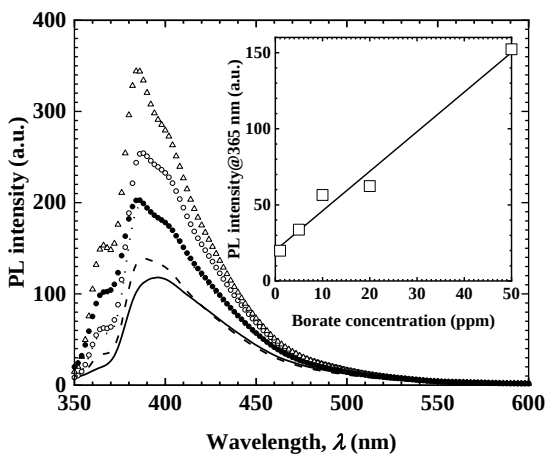


Fig. 5. PL spectra of CT(0.1)C_4S-LDH-sheet obtained after immersion in aqueous borate solutions of varying concentrations: 1.0 ppm (solid line), 5.0 ppm (broken line), 10.0 ppm (dotted line), 20.0 ppm (○), 50 (△), and 100 ppm (●). Inset: Borate concentration dependence of PL intensity at 365 nm for CT(0.1)C_4S-LDH-sheet.

We prepared a nonwoven fabric sheet loaded with LDH, CT, and C_4S anions (CT(x)C_4S-LDH-sheet) and investigated its ability to detect borate anions in aqueous solutions. CT(x)C_4S-LDH-sheet could detect borate anions in aqueous solutions. Specifically, the PL intensity of CT(0.1)C_4S-LDH-sheet at 365 nm linearly increased with borate anion concentration, indicating its potential for the quantitative detection of borate anions in aqueous solutions below 50 ppm. Further, CT(0.1)C_4S-LDH-sheet could detect borate anions at 10 ppm, corresponding to the effluent standards used in Japan. Thus, CT(0.1)C_4S-LDH-sheet demonstrated high potential as a borate-detection material suitable for practical wastewater applications. However, further investigations are required to assess its performance in the presence of other anion species, such as chlorides and sulfates, and exploring its applicability for detecting borate in complex environmental samples, such as wastewater or natural water bodies.

For the practical use of the CT(0.1)C_4S-LDH-sheet, we will investigate the potential of integrating it into portable sensing devices for onsite monitoring applications and its stability and long-term performance under different environmental conditions. Moreover, we plan to investigate the feasibility of detecting other contaminants and anions using similar hybrid materials to broaden the scope of the research. This study highlights the utility of LDH-loaded nonwoven fabric sheets as host materials for hybrid LDH-functional dye materials. Therefore, the practical applications of hybrid materials comprising LDH and functional dyes are expected to increase in the future.

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Supplementary data

Supplementary material is available at *Chemistry Letters*

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Conflict of interest statement. None declared.

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