1 Title

2 Luminous Relative Humidity Sensing by Anionic Fluorescein Dyes Incorporated into Layered Double
3 Hydroxide/1-Butanesulfonate Hybrid Materials

4 Author names and affiliations

5 Ryo Sasai^{*1,2} and Michio Morita^{†1}

6 1 Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, F3-3(250)
7 Chikusa-ku, Furo-cho, Nagoya 464-8603, Japan

8 *Corresponding author

9 e-mail address: rsasai@riko.shimane-u.ac.jp

10 Present address of RS

11 2 Department of Physics and Materials Science, Interdisciplinary Graduate School of Science and
12 Engineering, Shimane University, 1060, Nishikawatsu-cho, Matsue 690-8504, Japan

13 Abstract

14 Spectroscopic properties of solid relative humidity (RH) sensors consisting of anionic fluorescein dyes
15 (AFD) and 1-butanesulfonate (C4S) ions hybridized with layered double hydroxides (LDH) were
16 investigated under various RH conditions. The obtained LDH/C4S/AFD hybrid material contained at least
17 three different types of water adsorption sites with adsorption capacities of one water molecule per formula
18 unit. Photoluminescence (PL) intensity of the LDH/C4S/AFD hybrid was significantly enhanced by water
19 adsorption (especially in the RH range between 20 and 80%) indicating that the synthesized material
20 possessed strong RH sensing properties and thus could be used in water vapor sensor devices.

21 Keywords

22 Relative Humidity Sensing, Layered Double Hydroxide, Anionic Fluorescein, Hybrid Materials, Fluorescent
23 Dyes

Introduction

Controlling relative humidity (RH) is very important for various applications such as storage and transportation of precision instrument, cereal grain, and vegetables. In general, RH indicators must meet the following requirements: (i) should be stable over a broad range of humidity, (ii) should be non toxic, and (iii) should exhibit high contrast tone. Co compounds are well known for their sensing abilities and thus have been widely used for this purpose. However, Co represents a valuable metal of national strategic importance, and its compounds are not capable of quantifying RH in a given environment. Thus, practical humidity indicators characterized by the ability to quantitatively detect spatial RH are in high demand for various industrial needs.

Layered double hydroxides (LDH: $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, A^{n-} : n -valent anion, m : number of hydration water species) are promising hosts for hybrid materials with valuable properties due to the unique molecular aggregation structure formed by various functional groups incorporated into a 2-dimensional LDH interlayer nanospace via an anion-exchange reaction. LDH can generally adsorb large amounts of water, and its basal spacing value increases with an increase in RH. Moreover, small amounts of adsorbed water species exist in the interlayer nanospace, even when it is mostly occupied by organic compounds. Constantino et al. [1] have reported that photoluminescence (PL) properties of methyl orange incorporated into the LDH interlayer space were changed by water adsorption accompanied by hybrid material swelling. Mohanambe et al. [2] showed that PL properties of LDH/dodecylsulfate hybridized with pyrene were changed with varying RH of a particular environment. Shi et al. [3-5] studied PL of solid materials containing anionic fluorescein dyes (AFD) and surfactant anions hybridized with LDH, which could be potentially used as optical sensors for soluble organic compounds or pH indicators. Recently, we reported the preparation of solid materials with strong luminous properties obtained by hybridization of various dyes (such as rhodamine and fluorescein) with inorganic layered materials including saponite, laponite, layered titanate, and LDH [6-17]. Moreover, a few materials among our prepared solid hybrids exhibited a luminosity dependence on the composition and concentration of molecular species present in the surrounding environment [18].

In this study, spectroscopic properties of AFD molecules incorporated into LDH modified by 1-butanefulfonate (C4S) anions were investigated at various RH values, and a possible mechanism describing the PL response to the change in RH was discussed.

Experimental Procedures

Materials. MgAl layered double hydroxide (LDH: $[Mg_3Al(OH)_8]CO_3^{2-} \cdot nH_2O$, anion-exchange capacity (AEC): 3.25 mmol/g) was purchased from Kyowa Chemical Industry Co. Ltd. Anionic fluorescein dye (AFD) obtained from Tokyo Chemical Industry Co. Ltd. was used as a luminescent dye. Na 1-butanefulfonate (C4S) was purchased from Tokyo Chemical Industry Co. Ltd. All chemicals were used without further purification. Decarbonated water prepared by boiling distilled and deionized water was utilized in all experiments.

Preparation of solid LDH/AFD/C4S. LDH/AFD/C4S hybrid solid material was prepared by replacing acetate anions with AFD and C4S species in accordance with the ion exchange procedure described in our previous paper [17]. After taking into account the AEC of the utilized LDH, the

added amounts of AFD and C4S were set to 0.025% and 200%, respectively. The characterization of the prepared LDH/AFD/C4S powder was performed by various analytical procedures described elsewhere [17].

As a result, a greenish yellow LDH/AFD/C4S powder with a chemical composition corresponding to the formula $[\text{Mg}_3\text{Al}(\text{OH})_8](\text{AFD})_{0.00025}(\text{C4S})_{0.69}(\text{CO}_3)_{0.15} \cdot 2.98\text{H}_2\text{O}$ was successfully prepared under dry conditions.

Characterization of solid LDH/AFD/C4S under humid conditions. Water adsorption experiments as well as X-ray diffraction (XRD), PL quantum yield ϕ , and diffuse reflectance (DR) measurements were performed for the obtained LDH/AFD/C4S hybrid solid material at 25°C in accordance with the previously described experimental procedures [16]. PL properties of solid LDH/AFD/C4S were studied *in-situ* under Ar gas flow at various RH values (3–90%) and 25°C utilizing a custom-made PL measurement system depicted in Figure 1. PL spectra were recorded according to the following steps. (1) An LDH/AFD/C4S pellet was placed inside a sample quartz cell and treated with a stream of dry Ar gas with a flow rate of 30 cm³/min for 20 min. (2) A PL spectrum for the dried LDH/AFD/C4S pellet excited by a UV-LED irradiation apparatus ($\lambda = 365$ nm, KEYENCE, Japan) was recorded with a multichannel fiber spectrophotometer (Ocean Photonics). (3) Humid Ar gas, produced by passing dry Ar gas through a pure water medium, was injected into the sample quartz cell for 20 min at a flow rate of 50 cm³/min. (4) PL spectra for the resulting LDH/AFD/C4S pellet were recorded at various RH values, which were measured by a digital hygrometer.

Results and Discussion

Water adsorption by solid LDH/AFD/C4S. Figure 2 shows the dependence of the adsorbed water content on the RH value for the prepared LDH/AFD/C4S hybrid material, which consists of three main stages. First, the adsorbed water amount rapidly increases until the RH value reaches 30% followed by a more moderate increase in the RH region between 30% to 80%, while at RH > 80%, the amount of adsorbed water starts rapidly increasing again. The obtained results suggest the presence of at least three types of water adsorption sites on the LDH/AFD/C4S surface. The RH dependence of the ΔL parameter defined as $d_{003}(\text{RH} = x\%) - d_{003}(\text{RH} = 0\%)$, where d_{003} represents the d -spacing of the (003) XRD reflection observed in the inserted typical XRD pattern of the LDH/AFD/C4S hybrid materials at RH = 30 %, is shown in Figure 3. The obtained ΔL values drastically increase until reaching the size of a water molecule (0.28 nm) at RH of about 30% indicating the formation of an adsorbed water monolayer on the LDH nanosheet surface. At RH below 30%, the active water adsorption sites correspond to hydroxyl groups and anion exchange sites on the LDH surface and/or sulfuric groups of the C4S species incorporated into the LDH interlayer space. At RH above 30%, the ΔL magnitude slightly increases with an increase in RH up to 50% and then stabilizes at a level of about 0.3 nm. No changes in the interlayer distance were observed at RH values greater than 50%; however, the adsorbed water content continued to increase in this region (see Figure 2). The obtained data suggest that the water adsorption at RH above 50% occurred in hydrophobic cavities formed by the C4S species incorporated into the LDH interlayer space with an occupancy rate of about 35% (calculated from the molecular volume of C4S (0.19

nm³)) and interlayer volume per anion exchange site of about 0.37 nm³. The adsorbed water amount estimated from the remaining cavity volume was about 22 mol per formula unit, but the actual adsorbed water content (at RH of 96%) was equal to 5.5 mol per formula unit indicating that the water adsorption process observed at RH of above 50% corresponded to hydrophobic hydration.

Spectroscopic studies of solid LDH/AFD/C4S before and after water adsorption. Figure 4 shows the DR and PL spectra for the LDH/AFD/C4S solid material obtained under dry and wet (corresponding to RH of about 80%) conditions indicating that the obtained hybrid material is characterized by remarkable differences in spectroscopic features corresponding to the incorporated AFD chromophores, which are caused by varying the RH value (similar changes were observed for the absorption and PL spectra of AFD aqueous solutions with different pH; see Figures S1 and S2 in the Supplementary materials). Such spectral differences can be explained by the change in chemical equilibrium between dianionic, monoanionic, and nonionic AFD species caused by pH variations. It can be suggested that the dianionic and monoanionic forms of AFD are stabilized in the interlayer space of the LDH/AFD/C4S hybrid solid material under wet and dry conditions, respectively, because both the corresponding absorption and PL spectra match those recorded for AFD aqueous solutions with pH = 5 and 7. The dianionic AFD species become stable in the LDH/AFD/C4S hybrid material under wet conditions due to the formation of a basic interlayer space resulting from the water adsorption at increased pH (when the LDH species are dispersed in an aqueous solution). Meanwhile, the monoanionic AFD species are produced under dry conditions owing to the reduction in polarity of the LDH interlayer space caused by the desorption of hydrated water molecules. Therefore, it can be concluded that the presence of C4S molecules plays a very important role in the sharp decrease in polarity of the interlayer space. This conclusion is supported by the additional data indicating that the absorption and PL spectra of AFD species incorporated into an LDH/AFD hybrid solid material were not changed by varying the humidity conditions (see Figure S3 in the Supplementary materials).

PL properties of AFD species incorporated into solid LDH/AFD/C4S. Figure 5 shows the RH dependence of the PL enhancement rate, E , defined as $(I^{\text{RH}} - I^{\text{RH}=0}) / I^{\text{RH}=0}$, where $I^{\text{RH}=0}$ and I^{RH} are the intensities of the PL peak recorded at about 527 nm under dry conditions and at a specified RH value, respectively. The obtained E values remained constant at RH below 20% despite the significant water adsorption observed in the RH region below 30%, which could potentially cause a substantial enlargement of the interlayer distance (see Figures 2 and 3). Since water molecules can be adsorbed on the LDH layer surface below RH = 30%, they should not affect the luminous properties of the AFD species incorporated into the LDH/AFD/C4S hybrid solid material. The E values linearly increase with an increase in RH from 20% to about 80%. The adsorption of water molecules observed in this RH range occurs due to the hydrophobic field formed by the alkyl groups of the C4S species in the interlayer space; furthermore, the adsorbed water molecules can also be localized around the incorporated AFD species. As a result, monoanionic or nonionic AFD stabilized in the interlayer space under low RH conditions can be converted to dianionic AFD with an increase in RH. Finally, the PL enhancement rate reaches saturation at a RH of about 80%,

which can be explained by the conversion of all incorporated AFD molecules into dianionic AFD species.

Reversibility and iteration stability of luminous RH sensing properties. Figure 6 depicts the R values (defined as $I^{\text{wet}} / I^{\text{dry}}$) obtained under alternate dry and wet conditions. It was found that the structure conversion reaction of the AFD molecules incorporated into the LDH/AFD/C4S hybrid solid material, caused by the change between the dry and wet conditions, is reversible, because the R value for the initial dry state was identical to the dry R value obtained after a series of wet and dry operations. Additionally, such reversible reaction of AFD could be observed under all RH conditions. Furthermore, the stability of the luminous response for the studied hybrid material remained relatively high after several cycles of the dry and wet measurements. These observations indicate that the AFD photodegradation reaction can be inhibited by incorporating AFD species into the interlayer space of the LDH/C4S hybrid. However, the exact reason why the hybridization of AFD with LDH/C4S impedes the photodegradation of AFD under light irradiation remains unclear.

Conclusions

The prepared LDH/AFD/C4S hybrid solid material was found to possess luminous RH sensing properties, which can be quantified in the RH range between 20% and 80%, making the obtained hybrid suitable for optical RH sensor devices. The optical RH response of the LDH/AFD/C4S hybrid characterized by reversibility and high iteration stability was related to the molecular structural changes of incorporated AFD caused by the water absorption into the hybrid interlayer space. Meanwhile, the sensing ability of the present LDH/AFD/C4S hybrid solid material for other gas molecule such as organic vapor and inorganic gases is very interesting for us, and thus, we can show you the the sensing ability of the present LDH/AFD/C4S hybrid solid material for other gas molecule in the near future.

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Figure 1. A schematic diagram of the custom-made *in-situ* PL measurement system.

Figure 2. An RH dependence of the adsorbed water content.

Figure 3. An RH dependence of the ΔL parameter. The broken line denotes the hydrodynamic diameter of a water molecule (0.28 nm). Inserted figure is the typical XRD pattern of LDH/AFD/C4S hybrid in the presence of adsorbed water molecules in the interlayer space (RH = 30 %).

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Figure 4. DR (left axis) and PL (right axis) spectra for the LDH/AFD/C4S hybrid solid material. The solid lines represent the spectra recorded under wet conditions (at RH of about 80 %), while the broken lines denote the data obtained under dry conditions. The PL excitation wavelength was 480 nm.

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Figure 5. An RH dependence of the PL enhancement rate.

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Figure 6. PL intensity ratio ($R = I^{\text{wet}}/I^{\text{dry}}$) variations measured under dry and wet (RH = 80%) conditions.

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Graphical Abstract