Sensors and Actuators B 238 (2017) 702–705

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Luminous relative humidity sensing by anionic fluorescein dyes incorporated into layered double hydroxide/1-butanesulfonate hybrid materials

Ryo Sasai*, Michio Morita

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

A R T I C L E   I N F O

Article history:
Received 6 May 2016
Received in revised form 13 July 2016
Accepted 21 July 2016
Available online 22 July 2016

Keywords:
Relative humidity sensing
Layered double hydroxide
Anionic fluorescein
Hybrid materials
Fluorescent dyes

A B S T R A C T

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

1. 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: $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2](A^{n-})_{x/n}{}^{\bullet}mH_2O$, 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-butanesulfonate (C4S) anions were investigated at various RH values, and a possible mechanism describing the PL response to the change in RH was discussed.

---

* Corresponding author. Present address: Department of Physics and Materials Science, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060, Nishikawatsu-cho, Matsue, 690–8504, Japan.

E-mail address: rsasai@riko.shimane-u.ac.jp (R. Sasai).

http://dx.doi.org/10.1016/j.snb.2016.07.109
0925-4005/

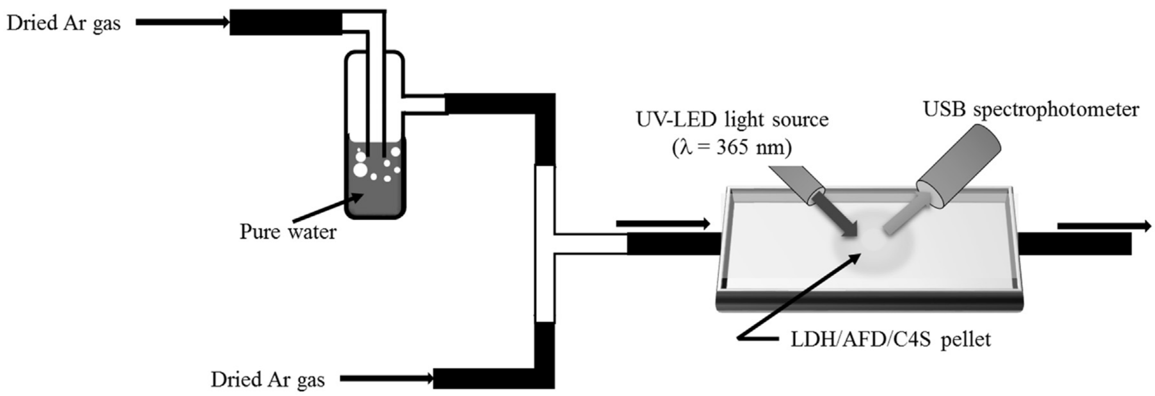

Fig. 1. A schematic diagram of the custom-made *in-situ* PL measurement system.

Experimental Procedures

1.1. Materials

MgAl layered double hydroxide (LDH: $[Mg_3Al(OH)_8]CO_3{}^{2-}\bullet nH_2O$, 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-butanesulfonate (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.

1.2. 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 $[Mg_3Al(OH)_8](AFD)_{0.00025}(C4S)_{0.69}(CO_3)_{0.15}\bullet 2.98H_2O$ 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 Fig. 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 cm^3/min for 20 min. (2) A PL spectrum for the dried LDH/AFD/C4S pellet excited by a UV – LED irradiation apparatus (λ = 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 cm^3/min. (4) PL spectra for the resulting LDH/AFD/C4S pellet were recorded at various RH values, which were measured by a digital hygrometer.

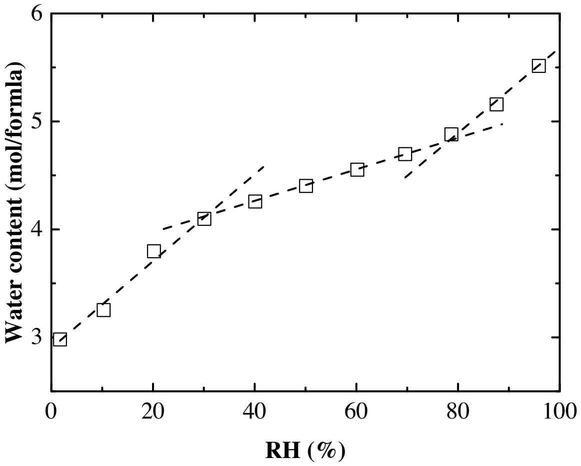

Fig. 2. An RH dependence of the adsorbed water content.

2. Results and discussion

Water adsorption by solid LDH/AFD/C4S

Fig. 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 $d_{003}(RH = x\ \%) - d_{003}(RH = 0\%)$, 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 Fig. 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,