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ARTICLE

Fluorescein Dyes Intercalated Layered Double Hydroxides for Chemically Stabilized Photoluminescent Indicators on Inorganic Surfaces

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A new photoactive thin film of layered double hydroxide (LDH) nanocrystals containing fluorescein dyes (LDH-F) has been developed by self-assembly of the LDH nanocrystals and well-controlled intercalation of the dyes under organic media. XRD results and absorption spectra confirmed the highly oriented interlayer arrangement of dianionic form of the fluorescein dyes in the LDH interlayers, in which the dye molecules were electrostatically immobilized between the positively charged LDH layers with a monolayer packing structure. An intensity weighted average PL lifetime was estimated to be 1.45 ns and a fluorescence lifetime image microscopy revealed that the individual LDH nanocrystals on the LDH-F film had largely similar lifetimes, which were ascribed to the uniform loading of fluorescein dyes into the LDH matrix without a photoluminescence quenching.

Introduction

The controlled organization of fluorescent organic dyes in a solid matrix offers numerous prospective applications in the field of chemical and biological sensing technologies.[1-3] Among the fluorescent dyes, fluorescein and its derivatives are commonly used as fluorescent indicators and sensors, due to their large extinction coefficients (90,000 $M^{-1}cm^{-1}$), high quantum yields (0.95), and chemical and biological stability.[4-7] These organic dyes show a high fluorescence efficiency in solution, but a significant fluorescence quenching rapidly occurs when they are aggregated in solid state. During the past two decades, layered double hydroxide (LDH) has attracted considerable attention as a two-dimensional host material to immobilize individual dye molecules in the LDH matrix.[8-11] The ordered structures and the surface charges of the LDH could effectively provide defined microscopic environments, a tunable loading density, and photostability of the fluorescent organic dyes.

The LDH consists of a continuous stack of positively charged metal hydroxide layers with counter anions and water molecules placed in the interlayer spaces. The stacking of the hydroxide layers in LDH is similar to that of brucite, $Mg(OH)_2$, in which magnesium cations are octahedrally bonded to six hydroxyl groups and these units are linked to each other through the edge sharing to form two-dimensional layers.[12] The chemical composition of the LDH is represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, capable of occupying the octahedral holes of brucite-like layers.[13-16] The

trivalent metal ions substitute isomorphically the divalent metal ions of the hydroxide layers, resulting in positive net charges that are compensated by hydrated anion (A^{n-}) in the interlayer spaces. A large variety of anions can be incorporated into the interlayer spaces of the LDH by anion exchange or intercalation procedure. Therefore, the unique layer structure of LDH and the binding property of anions in the interlayer space could facilitate the preparation of new organic-inorganic hybrid LDH materials with desired properties.

Recently, the LDH has practically allowed the photoactive coatings of the fluorescent organic dyes in the form of oriented films.[17-22] Iyi and co-workers have prepared porphyrin intercalated LDH films by a solvent-evaporation[21] and Wei and co-workers have used an electrophoretic deposition to form fluorescein co-intercalated LDH film.[22] Both methods have required the pre-intercalations with organic pillars of long alkyl chains to expand the LDH layers. In this work, we employed the crystallographically oriented thin film of the LDH nanocrystals as a solid matrix to organize the fluorescein dyes in the interlayer spaces of LDH nanocrystal by a monolayer particle-assembly and a direct anion-exchange procedure under organic media. This reaction allowed the monolayer packing of the individual fluorescein dyes in the LDH matrix, where the ordered microscopic structures of LDH matrix could provide the specific organization and the photostability of the fluorescein dyes, in which the individual LDH nanocrystals exhibited a characteristic photoemission of fluorescein dyes with a largely similar photoemission and a 1.45 ns of average photoluminescence lifetime. We now report the fabrication and

characterization of a new photoactive thin film of oriented LDH nanocrystals intercalated with fluorescent organic dyes on solid substrates. The photoemission properties of the film were demonstrated by using confocal fluorescence microscopy, time-resolved photoluminescence analysis and fluorescence lifetime image microscopy.

Experimental

Synthesis of carbonate-containing LDHs

$[Mg_4Al_2(OH)_{12}]CO_3 \cdot nH_2O$, LDH-carbonate, was prepared by co-precipitation. To an aqueous solution of 0.02 M $Mg(NO_3)_2 \cdot 6H_2O$ and 0.01 M $Al(NO_3)_3 \cdot 9H_2O$ a mixed solution of 2.0 M NaOH and 0.2 M Na_2CO_3 was slowly added under vigorous stirring. The pH of the solution was adjusted to 10.0 ± 0.1 at room temperature during the titration. The resulting precipitate was collected by centrifugation and washed three times with deionized water. Hydrothermal treatment was carried out in deionized water at 180°C to obtain larger crystals and improve the crystallinity of the LDH-carbonate. Samples were then dried at 120°C in a convection oven. The chemical analysis for Mg and Al in LDH-carbonate was carried out using an inductively coupled plasma optical emission spectrometer. The C and H contents were measured using an elemental analyzer, and the water content was determined from a thermo gravimetric analysis result. The chemical formula of the LDH-carbonate was $[Mg_{1.94}Al_{1.00}(OH)_{6.06}](CO_3)_{0.51} \cdot 2.06H_2O$.

Preparation of LDH-C and LDH-F films

10 mg LDH-carbonate was suspended in 20 mL 1-butanol, and then ultrasonicated (95 W, 28 kHz) at room temperature in the ambient atmosphere. The Si wafer substrates were cleaned with an oxygen plasma cleaner (Harrick, 30 W), immersed in a colloidal suspension of LDH-carbonate and treated by ultrasonication for 2 min. The LDH-coated substrates were ultrasonicated in the solvents without LDH for 1 min to rinse them and then dried at 70°C in air. To prepare the LDH-F film, thin film LDH-C was transferred into a Teflon-coated solvothermal reactor containing 20 mg of fluorescein and a mixture of ethanol/toluene. The films were washed with anhydrous ethanol several times and dried under air. To verify the optical properties of the LDH-C and LDH-F film, the samples were prepared on glass plates under the same reaction conditions.

Photoluminescence measurements

Photoluminescence spectrum has been measured using a commercial fluorometer (F-7000, Hitachi) with 400 nm excitation. The film sample has been applied against the excitation beam at the angle of 35° and a 430 nm long-pass filter in order to avoid any scattering. Time-resolved photoluminescence has been drawn at 550 nm using a time-correlated single photon counting method (FluoTime 200, PicoQuant, Germany) using a 485 nm diode laser with a 500 nm long-pass filter to block any scattered light. For fluorescence lifetime imaging microscopy (FLIM) measurements, we used a commercial FLIM setup (MicroTime 200; PicoQuant, Germany). A diode-pulsed laser (470 nm, 40 MHz, <1 μW, LDH-P-C-470B/PDL 800-B; PicoQuant) was used to excite fluorescein, and emissions from 500 to 800 nm were collected through the object in 40,000-pixel mode. FLIM data were analyzed using Symphotime64 software (PicoQuant).

Characterizations

XRD patterns were measured using a Rigaku X-ray diffractometer. The field emission scanning electron microscopy (FE-SEM) images were obtained on a JEOL 7401F (JEOL Ltd, Japan) operating at 30 kV. Before imaging, the samples were coated on carbon by sputtering with Pt to a thickness of about 3 nm. UV/Vis spectra were measured using a Lambda 1050 (Perkin Elmer, USA). Confocal microscopy images were obtained using a LSM710 (Carl Zeiss, German). Chemical analyses of Mg, Al and Se were carried out using an inductively coupled plasma atomic emission spectrometer (ICP-AES), JY Ultima2C (Jovin Yvon, France).

Results and discussion

Preparation and X-ray analysis of LDH-F film

The LDH powder with the formula $[Mg_4Al_2(OH)_{12}]CO_3 \cdot nH_2O$ (LDH-C), was synthesized using the coprecipitation method.[11,12] The resulting precipitate was hydrothermally treated to obtain a large crystal size and improve its crystallinity;[23] this was confirmed by XRD and SEM measurements as shown in Fig. 1 and Fig. 2a. The oriented LDH-C film was prepared on Si substrates by ultrasonic-treatment of the substrate in a 1-butanol containing the LDH-C powder. The bonding between LDH and Si substrate was ascribed to electrostatic attraction resulting from positively charged LDH particles and the negatively charged Si substrate.[24,25] The XRD pattern (Fig. 1) and SEM image (Fig. 2b) of the LDH-C film revealed a single particular layer of the well-attached LDH-C on the Si substrate with preferred orientation along the crystallographic c axis perpendicular to the substrate plane.
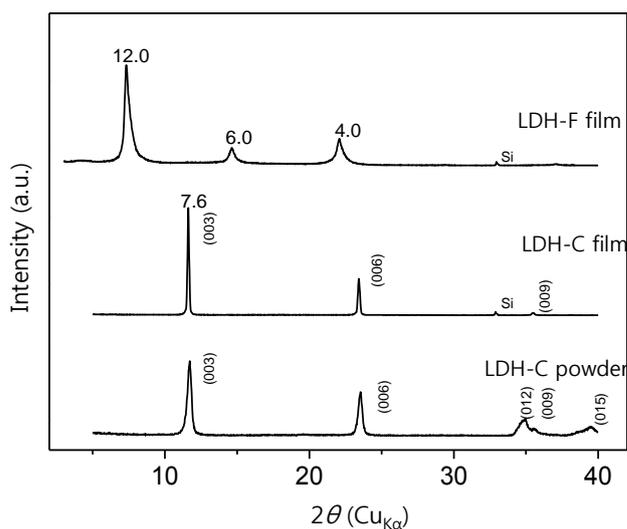
Fig. 1. XRD patterns of LDH-C powder, LDH-C film and LDH-F film. The unit of the d-values in (a) is Å.

The XRD of the LDH-C film corresponded to the pristine interlayer spacing (7.6 Å) of the interlayer carbonate ions,

which became larger spacings (12.0 Å) due to the anion exchange with fluorescein dyes as shown in the XRD pattern of Fig. 1. The thin film of LDH intercalated with the fluorescein dyes (LDH-F) was prepared by the treatment of the LDH-C film with fluorescein dyes in the ethanol/toluene mixture (1 %, v/v) at 120 °C for 48 hr. These conditions allowed the carbonates to be successfully replaced with the fluorescein molecules in the gallery spaces of the LDH-C. The interlayer distance of the fluorescein phase does not change with further reaction time. Under a reaction temperature lower than 100 °C or a reaction time shorter than 36 hr, the fluorescein dyes were partially incorporated into the LDH layers with a dominant carbonate phase in XRD measurements. We note that the current reaction conditions could efficiently protect the incorporation of carbonates from carbon dioxide. We also note that the intercalation of the fluorescein dyes could be effectively induced by the ethanol in the reaction media,[26,27] because the small amount of ethanol enabled solubility for the de-protonation of the fluorescein dyes to anionic form and for the fast diffusion of the fluorescein dye into the LDH interlayers without any structural damages on the LDH particles. The XRD pattern of the LDH-F film also shows the intense (00*l*) reflections, implying a highly oriented arrangement of intercalated fluorescein dyes in the LDH layers. Interestingly, the SEM observations indicated that the morphology and the lateral dimension of the LDH particles on the Si substrate were preserved after the intercalation of the fluorescein dye without particle detachment from the substrate (Fig. 2c). The SEM image of the LDH-F film in Fig. 2e showed the considerable anisotropic expansion of height, presumably because the fluorescein molecules lift LDH slabs perpendicular to the substrate plane. The sharp edges of LDH-F nanocrystals indicated that the anion-exchange reaction using a small amount of alcohol might have a little influence on the crystallinity of LDH layers.
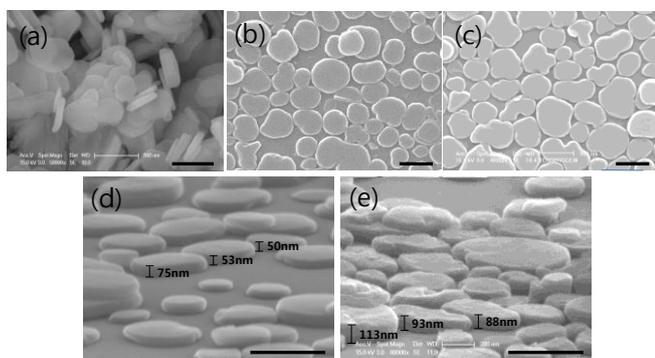
Fig. 2. SEM images of LDH-C powder (a), and the top-view of LDH-C film (b) and LDH-F film (c), and the tilted-view of LDH-C film (d) and LDH-F film (e). Scale bars: 500 nm.

The ionic characteristic of the fluorescein plays an important role in their intercalation chemistry and interlayer arrangement in the LDH matrix. Fig. 3 presents the molecular structures of the neutral and ionic forms of fluorescein dyes, and the possible interlayer conformation of the dye anions in LDH. The

fluorescein dye has several ionic species, from monovalent cation to divalent anion, depending on the solution pH as shown in Fig. 3a. The acid-base properties of the fluorescein are expressed by three equilibria[28] of $pK_1 = 1.95$, $pK_2 = 5.05$, and $pK_3 = 7.00$. The neutral form prevails in the range of $pK_1 < pH < pK_2$, and the monoanion and the dianion are present in the range of $pK_2 < pH < pK_3$ and at $pH > pK_3$, respectively. Considering the dianionic property of the fluorescein dyes at $pH > 7.0$[28,29], and the intercalation chemistry of the LDH based on the intrinsic surface charges and the basicity of the hydroxide layers with an isoelectric point at pH 11[30], the dyes could be readily deprotonated into dianions and stabilized between the positively charged hydroxide layers during the intercalation reaction. The interlayer distance of LDH-F was calculated by subtracting the LDH layer thickness, assumed to be a 4.8 Å. The observed value of 12.0 Å in XRD data corresponds to the 7.2 Å of interlayer spacing for the fluorescein dianion. Fig. 3c shows the probable conformation of the fluorescein dye anion in the interlayer regions, obtained with a Hyperchem program that gave a 7.3 Å of inter-atomic distance between the two anionic positions in the fluorescein dianion. This result is also in agreement with the inter-atomic distance in the fluorescein molecule from the crystallographic data (~7 Å).[31-33] This calculation suggested the single-layered disposition of the fluorescein dyes in the interlayer regions of the LDH matrix.
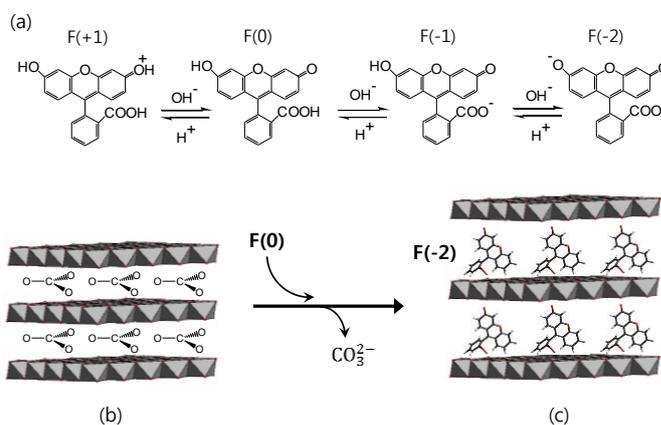
Fig. 3. Structures of neutral and ionic forms of fluorescein (a). Schematic representations of the intercalation reaction and the possible interlayer conformation of LDH-C (b) and LDH-F (c). The geometry is optimized by an Ab initio method (using a STO-3G parameter).

UV/Vis absorption and emission spectra

The intercalation of the fluorescein dyes in the LDH interlayers was investigated by the absorption spectra of the dyes in aqueous solutions and in the LDH matrix. Fig. 4a shows the absorption spectra of fluorescein recorded in aqueous solution at different pH values to determine the absorbance changes in their acid-base equilibrium. The cation form of fluorescein dye (F(+1) in Fig. 3a) showed the absorption maximum in the range of 430-440 nm, which was shifted to 491 nm at pH = 9.3. This visible transition occurred due to the change of the fluorescein

dyes into a dianion form[34-36] (F(−2) in Fig. 3a). It was reported that a pure solid fluorescein disodium salt showed the absorption maximum at 550 nm and its absorption was about 50 nm red-shifted when compared to the solution phase,[37] because of strong intermolecular chromophore-chromophore interactions in the pure solid state. In the case of fluoresceins bound to the surface of solid particles, the dyes showed a absorption similar to that of the solution of monoanionic form.[37] Dominantly, the LDH-F film on the glass plate shows sharp and intense visible absorption similar to the case of F(−2) in solution and its absorption maximum is located between that of the pure solid and the solution phases. Moreover, the absorption spectrum of the LDH-F film does not show the significant red-shift caused by a strong intermolecular interactions presented in a pure solid fluorescein disodium salt. This result strongly indicated that the intercalated dyes are in the dianion form and that they are electrostatically immobilized between the positively charged LDH layers. The LDH-C film has no characteristically visible absorption, whereas the inset photograph in Fig. 4b shows the uniform pale-yellow color of the LDH-F film, demonstrating the successful intercalation reaction of the fluorescein dyes throughout the entire surfaces of the LDH-F film.
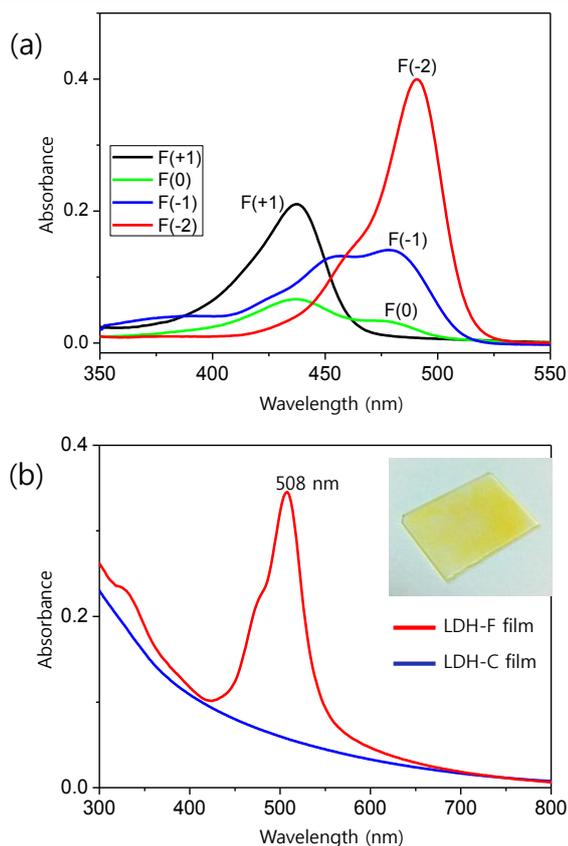
Fig. 4. UV/Vis absorption spectra for the individual neutral and ionic forms of fluorescein dyes (a) under aqueous solutions at pH 1.6; F(+1), pH 3.5; F(0), pH 5.5; F(-1) and pH 9.3; (F-2), and for LDH-C and LDH-F film (b). Inset in (b) shows a photograph of LDH-F film prepared on a glass plate. The LDH-C and LDH-F film were prepared on glass plates under the same reaction conditions.

The interlayer arrangement of the fluorescein dyes in the LDH matrix is crucial for exhibiting their characteristic photoemission with high fluorescence efficiency. Fig. 5a shows emission spectra of the fluorescein dianions in LDH-F film (red line) and in aqueous solution (black line). The dyes in solution exhibited a single-molecular luminescence behavior. The LDH-F film had a broad half-bandwidth and the 18 nm of red-shifted emission compared with the solution sample, which was probably ascribed to the partial increase in intermolecular interactions when the dyes were incorporated into the LDH interlayers. However, importantly the main emission of the LDH-F film was due to the dianionic form of fluorescein dyes attached to the LDH interlayers. We also applied confocal fluorescence microscopy to specify the fluorescence properties of the LDH-F film as shown in Fig. 5b and 5c. The fluorescence microscopy gave important insight into the spatial distribution of the fluorescein dianions on the anion-exchanging sites in the LDH nanocrystals. The LDH-F crystals on the glass substrate strongly exhibited the characteristic emission of the fluorescein dyes in contrast to the uncovered regions of the glass plate. The intense fluorescence signals from the individual LDH-F crystals indicated the homogeneous distribution of the fluorescein dyes throughout the LDH nanocrystals. The results demonstrated that the LDH nanocrystals on the film could offer a confined and chemically stable environment for the immobilization of the fluorescein molecules without a significant fluorescence quenching, which is strongly related to the monolayer packing of the individual dye molecules in the interlayer spaces of the LDH crystals in the LDH-F film.
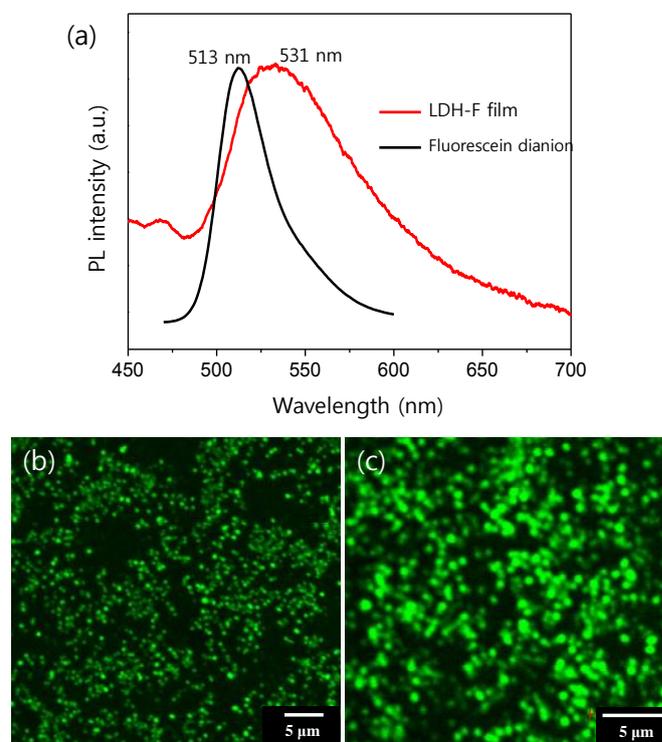
Fig. 5. Photoluminescence spectra (a) of fluorescein diaion (black line) in aqueous solution and LDH-F film (red line). Low (b) and high (c) magnification of

confocal fluorescence microscopy images of LDH-F film. The LDH-C and LDH-F film were prepared on glass plates under the same reaction conditions.

Fluorescence lifetime image microscopy (FLIM)

To monitor the relaxation dynamics of the LDH-F film, we conducted time-resolved photoluminescence (TR-Pl) measurement and convoluted using three exponential functions and instrumental response functions in Fig. 6. The convoluted parameters of five different spots of the LDH-F film are listed in Table S1. The intensity weighted average PL lifetime was estimated to be 1.45±0.13 ns, which is much shorter than the intrinsic PL lifetime of fluorescein dianion (3~4 ns). The shorter two time components of 0.2 ns (τ_1) and 1.1 ns (τ_2) were more than 97% and the remaining (τ_3) is negligible (<3%). The shorter two time components of 0.2 ns and 1.1 ns were more than 97% and the remaining is negligible (<3%). The shortened lifetime of the dye may be originated from the PL quenching by partial exciton/electron transfers to the neighboring molecules.
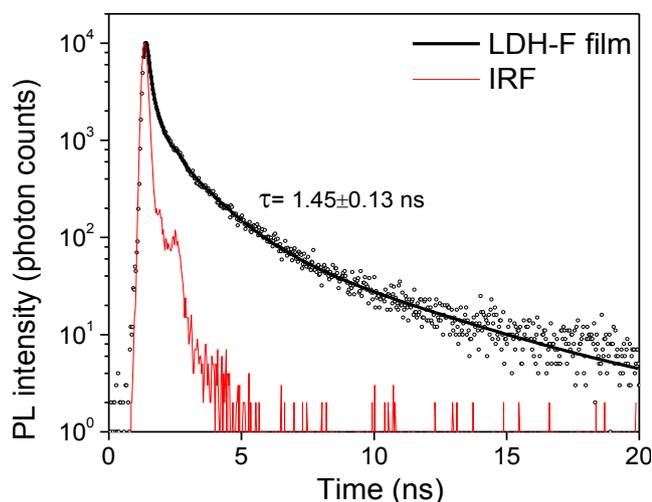
Fig. 6. Time-resolved photoluminescence trace of LDH-F- film at 550 nm using a 485 nm excitation. The TR-Pl trace was clearly discriminated from the instrumental response function (IRF) and was convoluted and averaged to have 1.45±0.13 ns. All the convoluted parameters are listed in Table S1.

In addition, we observed the fluorescence lifetime image microscopy (FLIM) technique to explore the quenching process in the LDH-F film as shown in Fig. 7. The FLIM image shows clear shape of individual particles with *ca.* 500 nm in diameter, which is much larger than the optical resolution (*ca.* 250 nm) of the confocal microscope. The FLIM images (low and high magnification) dominantly explained that the particles had largely similar lifetimes (colors in Fig. 7), implying that the dyes were not perturbed by self-aggregations and surface trap states and that the dyes were under similar environments even on the particle edges within this microscopic resolution. Therefore, the very thin layer of the LDH film containing the well-organized fluorescein dyes showed the homogeneous and strong photoemission from the individual LDH nanocrystals that can be virtually useful as a nanometer-sized fluorescent indicator due to the unique host-guest interactions of the LDH.

In addition, the current method provided a new type of photoactive coating of the fluorescent organic dyes in the form of the particulate thin films that can be widely applied to flat or non-flat substrates.
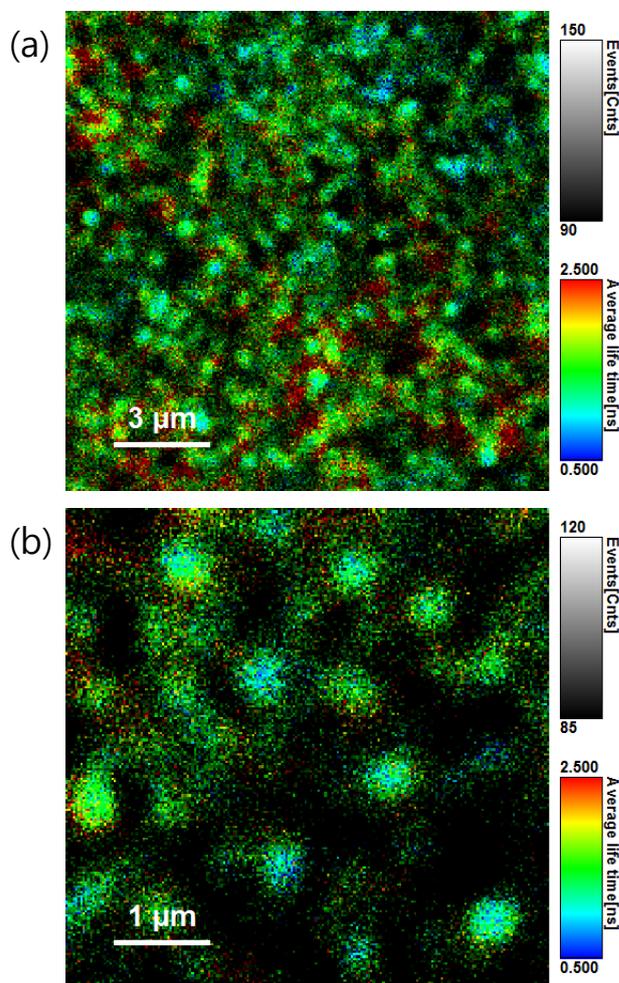
Fig. 7. Fluorescence lifetime imaging microscopy image of LDH-F- film with the resolution of 250 nm using a water emersion 1.4 numerical aperture objective. Time per pixel: 1.0 ms (a) and 0.6 ms (b).

Conclusions

The oriented photoactive thin film of the LDH particles intercalated with fluorescein dyes has been developed by well-controlled intercalation reaction under mixed organic solvents, in which the dye is chemically stabilized with a monolayer structure in the interlayer surfaces of LDH. The absorption spectra of the LDH-F film revealed the dianion form of the dye was intercalated in the LDH matrix. The intensity weighted average PL lifetime was estimated to be 1.45 ns. The FLIM measurements revealed the discrete LDH particles had almost similar lifetimes, which means that the most particles were not quenched by self-aggregation and surface traps. Combining the advantages of the controlled assembly of LDH nanocrystals and the anion stability of LDH matrices with photoactive molecules, the presented hybrid film can contribute to the area-selective

photochemical sensors based on the host-guest interactions of LDH.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: [Table S1. Fluorescence Property of fluorescein dyes intercalated LDH film]. See DOI: 10.1039/b000000x/

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Graphical Abstract

Fluorescein Dyes Intercalated Layered Double Hydroxides for Chemically Stabilized Photoluminescent Indicators on Inorganic Surfaces

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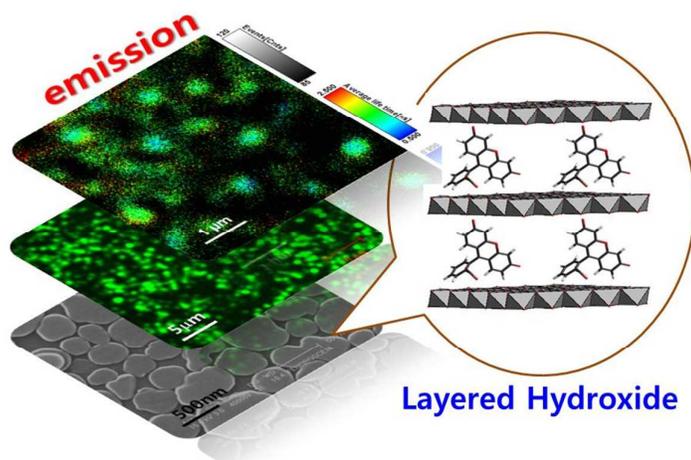
Thin film of LDH intercalated with fluorescein exhibits intense photoemission with uniform lifetime from individual LDH nanocrystals.