



HAL
open science

Observation of stacking faults and photoluminescence of laurate ion intercalated Zn/Al layered double hydroxide

Kenshi Harada, Thi Kim Ngan Nguyen, Yoshio Matsui, Kazuko Fujii, Fabien Grasset, Naoki Ohashi, Motohide Matsuda, Tetsuo Uchikoshi

► To cite this version:

Kenshi Harada, Thi Kim Ngan Nguyen, Yoshio Matsui, Kazuko Fujii, Fabien Grasset, et al.. Observation of stacking faults and photoluminescence of laurate ion intercalated Zn/Al layered double hydroxide. *Materials Letters*, 2018, 213, pp.323-325. 10.1016/j.matlet.2017.11.054 . hal-02160568

HAL Id: hal-02160568

<https://hal.science/hal-02160568v1>

Submitted on 30 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

Observation of stacking faults and photoluminescence of laurate ion intercalated Zn/Al layered double hydroxide

Kenshi Harada, Thi Kim Ngan Nguyen, Yoshio Matsui, Kazuko Fujii, Fabien Grasset, Naoki Ohashi, Motohide Matsuda, Tetsuo Uchikoshi

PII: S0167-577X(17)31679-8
DOI: <https://doi.org/10.1016/j.matlet.2017.11.054>
Reference: MLBLUE 23420

To appear in: *Materials Letters*

Received Date: 11 August 2017
Revised Date: 3 November 2017
Accepted Date: 11 November 2017

Please cite this article as: K. Harada, T.K.N. Nguyen, Y. Matsui, K. Fujii, F. Grasset, N. Ohashi, M. Matsuda, T. Uchikoshi, Observation of stacking faults and photoluminescence of laurate ion intercalated Zn/Al layered double hydroxide, *Materials Letters* (2017), doi: <https://doi.org/10.1016/j.matlet.2017.11.054>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Observation of stacking faults and photoluminescence of laurate ion intercalated Zn/Al layered double hydroxide

Kenshi Harada^{a,b}, Thi Kim Ngan Nguyen^{a,c,d}, Yoshio Matsui^a, Kazuko Fujii^a, Fabien Grasset^{a,d}, Naoki Ohashi^{a,d}, Motohide Matsuda^{b*} and Tetsuo Uchikoshi^{a,c,d*}

^aResearch Center for Functional Materials, National Institute for Materials Science, Tsukuba, Japan.

^bGraduate School of Science and Technology, Kumamoto University, Kumamoto, Japan.

^cGraduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan.

^dLaboratory for Innovative Key Materials and Structures, UMI 3629 CNRS-Saint Gobain-NIMS, NIMS, Tsukuba, Japan

*Corresponding authors

Tetsuo Uchikoshi: Tel: +81-29-859-2460, uchikoshi.tetsuo@nims.go.jp

Motohide Matsuda: Tel: +81-96-342-3726, mm_2008@alpha.msre.kumamoto-u.ac.jp

(Abstract)

NO₃-type Zn/Al layered double hydroxides were synthesized by co-precipitation method. The interlayers of the layered double hydroxides were highly expanded by intercalating laurate ions by ion exchange to get it easier to distinguish each layer of the layered double hydroxides by high-resolution transmission electron microscopy observation. Direct observation of the stacking faults in the expanded LDH was successfully carried out by intercalating the laurate ions. The expanded LDH exhibited photoluminescence under the irradiation of 325 nm UV light.

Keywords: Ceramics; LDH; Defects; Microstructure; Intercalation; Photoluminescence

1. Introduction

Layered double hydroxides (LDHs), which consist of two-dimensional (2D) stacking structures, are so-called clay minerals having anion exchange properties, and widely known as host materials in composite materials [1, 2]. Because of their advantages, such as being easy to prepare, high stability in air, significant anion-exchange property, and diversity of constituent elements, LDHs have been used for technological applications in variety of fields including catalyst, medicine, gas sorption, and fire retardants [3-6]. In general, LDHs are represented by the general formula $[M^{2+}_{(1-x)}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$, where $M^{2+} = Mg, Zn, Ca, Co, Fe, Ni, Cu, Li, \text{etc.}$, $M^{3+} = Al, Fe, Cr, Ga, \text{etc.}$, x is the charge density value of the hydroxide layer, $A^{n-} = Cl^-, CO_3^{2-}, NO_3^-, \text{etc.}$ [3-4,21], n is the formal charge of anion, and m is an amount of water molecules [22]. LDHs have

positively-charged metal hydroxide layers, in which the anions are stabilized in order to compensate the positive layer charges. Actual LDHs, however, would not be ideally-structured but could partly contain many defects. Recently, it has been pointed out that the defects in the layer structure of layered zinc hydroxide lead to photoluminescence (PL) [7]. Zhang et al. and Xu et al. have observed the PL of exfoliated Zn/Al LDH and Mg/Al LDH in a formamide solvent, and concluded that numerous surface defect sites may be responsible for the PL observed [8, 9]. However, no supporting results have been shown for the existence of defects in the previous reports. Sławiński et al. have reported the existence of stacking faults in the LDHs composed of $\text{Ni}_{0.67}\text{Cr}_{0.33}(\text{OH})_2(\text{CO}_3)_{0.16}\cdot m\text{H}_2\text{O}$ (3D structure) and $\text{Mg}_{0.67}\text{Al}_{0.33}(\text{OH})_2(\text{NO}_3)_{0.33}$ (2D layered structure) by powder XRD analysis [10]. Although being an effective method to study microstructures including defects, high-resolution transmission electron microscopy (HRTEM) has been limited in the use to confirm their plate-like shapes and survey the interlayer spacing for LDH [11-15]; there seems to be no report showing actually the existence of stacking faults by observation. In considering the previous reports, it must be significant to make a direct observation of stacking faults for further study. The authors have synthesized NO_3 type Zn/Al LDH by co-precipitation method; the interlayers of the LDH synthesized can be expanded by intercalating long chain organic anions between the metal hydroxide layers by ion exchange method. The purpose of the expansion is to get it easier to distinguish single layer of the LDH by HRTEM observation. In this report, structural defects of the LDH expanded by laurate ion whose chain size is about 1.7 nm were characterized by HRTEM observation. In addition, PL measurements were made for the laurate ion-intercalated LDH for further characterization of the defects.

2. Experimental

Regent grade $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, sodium nitrate (KISHIDA CHEMICAL Co., Ltd.) and sodium laurate (Nacalai Tesque Inc.) were used as raw materials without further purification. The Zn/Al LDH was prepared by co-precipitation method under nitrogen atmosphere to avoid the contamination of carbonates between the LDH layers. An aqueous mixed solution (42 mL) containing $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.028 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.014 mol) was continuously added dropwise to 1M NaNO_3 aqueous solution (140 mL) with stirring at room temperature. The pH value of the mixed solution was adjusted at pH=10 throughout the precipitation by adding 1 M NaOH aqueous solution. The precipitate was centrifuged at 15000 rpm for 10 min to remove the supernatant liquid and then washed with distilled water several times. The resulting white slurry was dried at 50°C. The prepared NO_3 -type Zn/Al LDH powder (0.1 g) was dispersed in distilled water (10 mL), and then a few drops of 1 M NaOH aqueous solution were added to adjust the pH of the slurry at about 10. After that, 0.1 M sodium laurate solution (10 mL) was added and the mixture was stirred for about 15 hours.

X-ray powder diffraction (XRD) analyses were carried out on a Rigaku MiniFlex600 diffractometer with CuK α radiation ($\lambda=1.5418 \text{ \AA}$), using the operation voltage and current of 40 kV and 15 mA, respectively. Fourier transform infrared (FT-IR) spectra were measured on an ATR PRO 450-S spectrometer in the range of 800–4000 cm^{-1} using the KBr pellet technique. HRTEM analysis was carried out on a JEOL JEM-2100F at 200 kV in bright field imaging. A micro PL system (Horiba, LabRAM HR) with a 325 nm He-Cd laser system was used to record the photoemission peaks in the wavelength range 350 nm and 1000 nm. The PL measurement was conducted several times on the same sample.

3. Results and discussion

XRD patterns of the synthesized NO₃-type Zn/Al LDH before and after the reaction with sodium laurate solution are shown in Fig. 1. The XRD pattern of the NO₃-type Zn/Al LDH displays typical diffraction peaks based on a nitrate form of the LDH indexed with rhombohedral symmetry ($d_{003}=0.89 \text{ nm}$) [2, 16]. A pronounced change was observed in the XRD pattern after the reaction: the XRD peaks shifted to lower 2θ angle compared with the NO₃-type Zn/Al LDH. The low angle pattern is shown in Fig. 1 (b). These peaks are indexed as (00 l) diffractions; therefore, it was identified as expanded-LDH intercalated by laurate ions ($d_{003}=3.87 \text{ nm}$). It was concluded that the use of the laurate ions attain high effectiveness in expanding the distance of LDH.

Fig. 1

FT-IR spectra of the NO₃-type Zn/Al LDH and the expanded-LDH are shown in Fig. 2. The FT-IR spectrum of the NO₃-type Zn/Al LDH presents broad absorption peaks in the wavelength range of 3200–3600 cm^{-1} and at 1620 cm^{-1} , which are assigned to the O-H stretching absorption of the hydroxide layers and the deformation vibration of the interlayer water molecules, respectively. The interlayer NO₃⁻ ions give a strong absorption band at 1385 cm^{-1} [2, 16]. The FT-IR spectrum of the expanded-LDH shows absorption peaks at 2800–3000 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of methyl and methylene groups, respectively. In addition, two other peaks at 1540 and 1410 cm^{-1} are associated to the asymmetric and symmetric carboxylate stretching vibrations [17, 23]. The absorption around 800 cm^{-1} is due to metal-oxygen vibrations [16, 20]. Those characteristic absorption peaks observed for the expanded LDH clearly indicate the presence of laurate ions in the samples measured, proving that the interlayers of LDH were expanded with the intercalation of laurate anions. Moreover, from the value of the basal spacing determined as 3.87 nm by XRD measurement, it is considered that two molecules of laurate ions with 1.7 nm in a longitudinal size [18] are upright present between the hydroxide layers of which the thickness was 0.48 nm [19]. In Fig. 1, a schematic is shown for double layers consisting of intercalated laurate ions between the hydroxide layers.

Fig. 2

Figure 3 shows an HRTEM image of the expanded-LDH with the intercalation of laurate ions. The dark and bright stripes represent hydroxide layers and laurate ion layers, respectively. The TEM

Fig. 3

observation provides direct evidence of the formation of layered structures and a defective part: Not only ideal layered structures but also the existence of a stacking defect are obviously confirmed inside the LDH. Our result would be the first case that a stacking defect in an LDH was directly observed by HRTEM.

Photoluminescence spectra of the expanded-LDH measured at the n -times, NO_3 -type LDH, and sodium laurate molecules are shown in Fig. 4. Emission peaks at approximately 400 nm and 440 nm were confirmed with all the expanded-LDH samples by the irradiation of the 325 nm He-Cd laser light. In addition, the photoluminescent intensity of the expanded-LDH was obviously stronger than that of the NO_3 -type LDH and the sodium laurate molecules. According to the previous reports [7-9], the reason was probably due to the presence of a lot of defects in the expanded LDH which would be induced by the interaction between the heterogeneous substances (LDH and laurate ion). As mentioned in the introduction, Zhang et al. and Xu et al. have reported the phenomenon that both the Zn/Al LDH ($\text{Zn/Al} = 4$) and Mg/Al LDH colloids containing their exfoliated nanoparticles exhibited photoluminescent emission spectra at 417 and 441 nm, respectively, under the irradiation of 378 nm UV light due to the increased surface defects resulting from the significant exfoliation [8, 9]. Our results give out that similar photoluminescent phenomenon is obviously detected by expanding the interlayer of the LDH even without exfoliation. Interestingly, the PL intensity decreased when the photoluminescence measurements of the same sample were repeated; the energy of excitation laser might influence on the LDH and/or the intercalated laurate ions.

Fig. 4

4. Conclusions

Defects in Zn/Al LDH were investigated by HRTEM observation. HRTEM observation of the expanded-LDH showed multilayer structure. In addition, defects with disordered stacking could be observed. PL measurement of the expanded-LDH showed very strong emission than those of the sodium laurate and nitrate LDHs. It was probable that the PL was observed due to the introduction of the defects in the LDH structure. However, the PL was weakened by repeating the measurements.

Acknowledgment

This study was carried out as part of the France-Japan international collaboration framework through the Laboratory for Innovative Key Materials and Structures (UMI 3629-LINK Center). The study was financially supported by the National Institute for Materials Science (NIMS), Kumamoto Univ., Saint-Gobain (France) and CNRS. The authors wish to thank David Lechevalier of Saint-Gobain KK (Tokyo, Japan) involved in LINK and related activities.

References

- [1] Z. P. Xu, P. S. Braterman, K. Yu, H. Xu, Y. Wang, C. J. Brinker, *Chem. Mater.*, 16, 2750-2756 (2004).
- [2] T. Tanaka, S. Nishimoto, Y. Kameshima, J. Matsukawa, Y. Fujita, Y. Takaguchi, M. Matsuda, M. Miyake, *J. Solid State Chem.*, 183, 479-484 (2010).
- [3] G. Fan, F. Li, D. G. Evans, X. Duan, *Chem. Soc. Rev.*, 43, 7040-7066 (2014).
- [4] U. Costantino, M. Nocchetti, M. Sisani, R. Vivani, *Z. Kristallogr.*, 224, 273-28 (2009).
- [5] Y. Tokudome, N. Tarutani, K. Nakanishi, M. Takahashi, *J. Mater. Chem. A*, 1, 7702-7708 (2013).
- [6] E. N. Kalali, X. Wang, D. Wang, *J. Mater. Chem. A*, 3, 6819-6826 (2015).
- [7] S. Yamashita, T. Shirai, M. Fuji, C. Takai, *Annual Report Adv. Ceram. Res. Ctr. Nagoya Inst Tech*, 1, 29-33 (2012).
- [8] Z. Zhang, G. Chen, K. Xu, *Ind. Eng. Chem. Res.*, 52, 11045-11049 (2013).
- [9] K. Xu, Z. Zhang, G. Chen, J. Shen, *RSC. Adv.*, 4, 19218-19220 (2014).
- [10] W. A. Sławiński, A. O. Sjøstad, H. Fjellvåg, *Inorg. Chem.*, 55, 12881-12889 (2016).
- [11] Z. Gu, A. C. Thomas, Z. P. Xu, J. H. Campbell, G. Q. M. Lu, *Chem. Mater.*, 20, 3715-3722 (2008).
- [12] L. Li, R. Ma, Y. Ebina, K. Fukuda, K. Takada, T. Sasaki, *J. Am. Chem. Soc.*, 129, 8000-8007 (2007).
- [13] L. Zhang, C. Dai, X. Zhang, Y. Liu, J. Yan, *Trans. Nonferrous Met. Soc. China*, 26, 2380-2389 (2016).
- [14] M. Eili, K. Shameli, N. A. Ibrahim, M. B. Ahmad, W. M. Z. W. Yunus, *J. Industrial Eng. Chem.*, 22, 63-69 (2015).
- [15] J. Plank, Z. Dai, P. R. Andres, *Mater. Lett.*, 60, 3614-3617 (2006).
- [16] S. Aisawa, S. Sasaki, S. Takahashi, H. Hirahara, H. Nakayama, E. Narita, *J. Phys. Chem. Solids*, 67, 920-925 (2006).
- [17] T. Nogueira, R. Botan, F. Wypych, L. Lona, *J. Appl. Polymer Sci.*, 124, 1764-1770 (2012).
- [18] K. Ueda, S. Inafuku, I. Mori, *Chemical Education*, 40, 114-117 (1992).
- [19] S. Gago, M. Pillinger, T. M. Santos, I. S. Gonçalves, *Ceramics-Silikáty*, 48, 155-158 (2004).
- [20] E. Y. Salih, Z. Abbas, S. H. H. A. Ali, M. Z. Hussein, *Adv. in Mater. Sci. and Eng.*, 2014, 647120, (2014).
- [21] A. Chroneos, K. Desai, S. E. Redfern, M. O. Zacate, R. W. Grimes, *J. Mater. Sci.*, 41, 675-687 (2006)
- [22] A. Motta, M-P. Gaigeot, D. Costa, *J. Phys. C*, 116, 12514-12524 (2012)
- [23] D. Tunega, H. Paalic, M.H. Gerzabek, H. Lischka, *J. Phys.: Condens. Matter*, 23, 404201 (2011)

Figure Captions:

Fig. 1 XRD patterns of the NO_3 -type Zn/Al LDH (a) before and (b) after the reaction with sodium laurate solution. Inserted figure shows the low angle XRD pattern of the NO_3 -type Zn/Al LDH treated with sodium laurate solution. The schematic illustrated in Fig. 1 shows the composite structure consisting of LDH and laurate ions estimated from XRD results and FT-IR spectra shown in Fig. 2

Fig. 2 FT-IR spectra of (a) NO_3 -type Zn/Al LDH and (b) LDH expanded by reaction with sodium laurate solution.

Fig. 3 HRTEM image of the expanded-LDH with intercalation of laurate ions.

Fig. 4 PL spectra of (a) expanded-LDH measured at the n-times, (b) sodium laurate, and (c) NO_3 -type LDH, respectively.

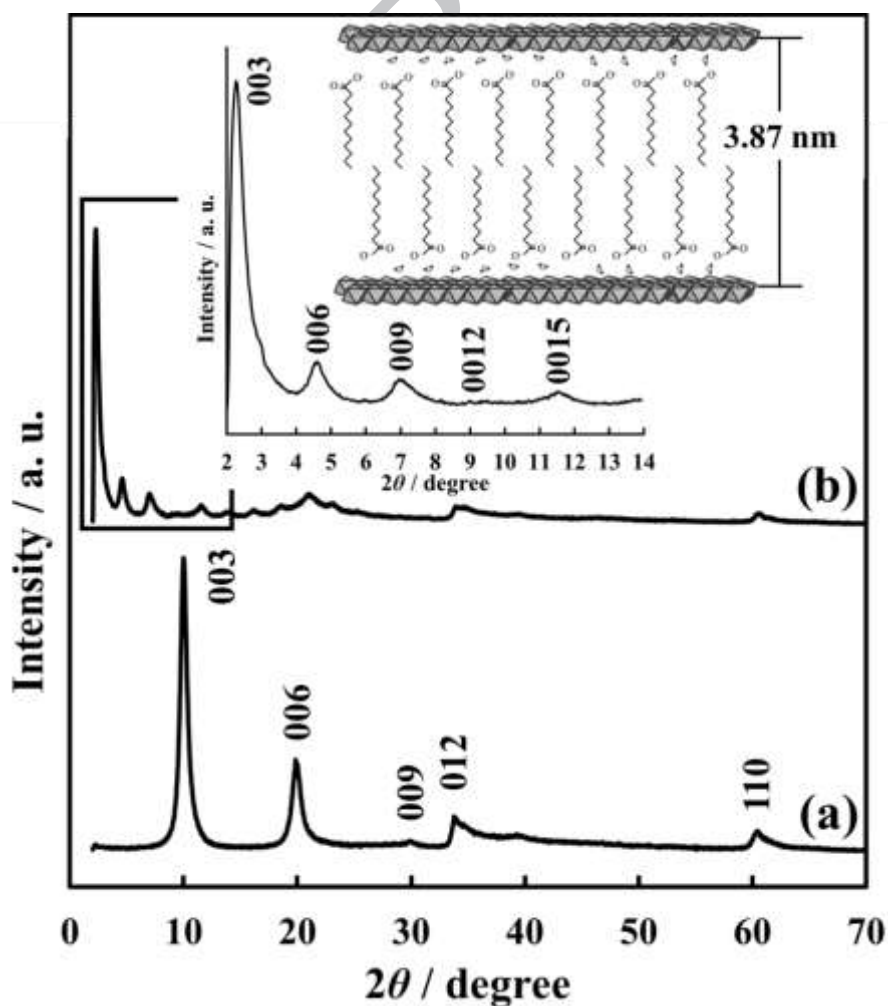
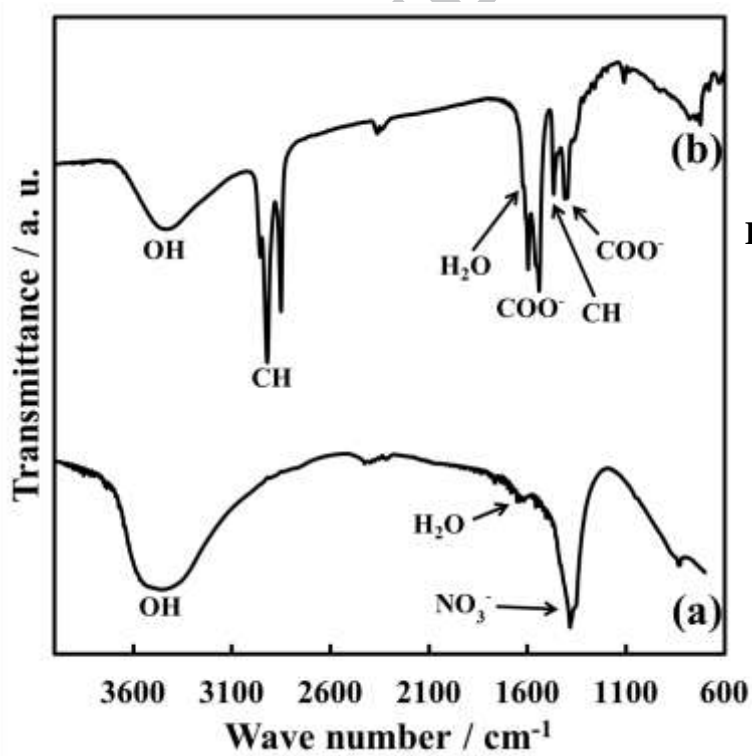
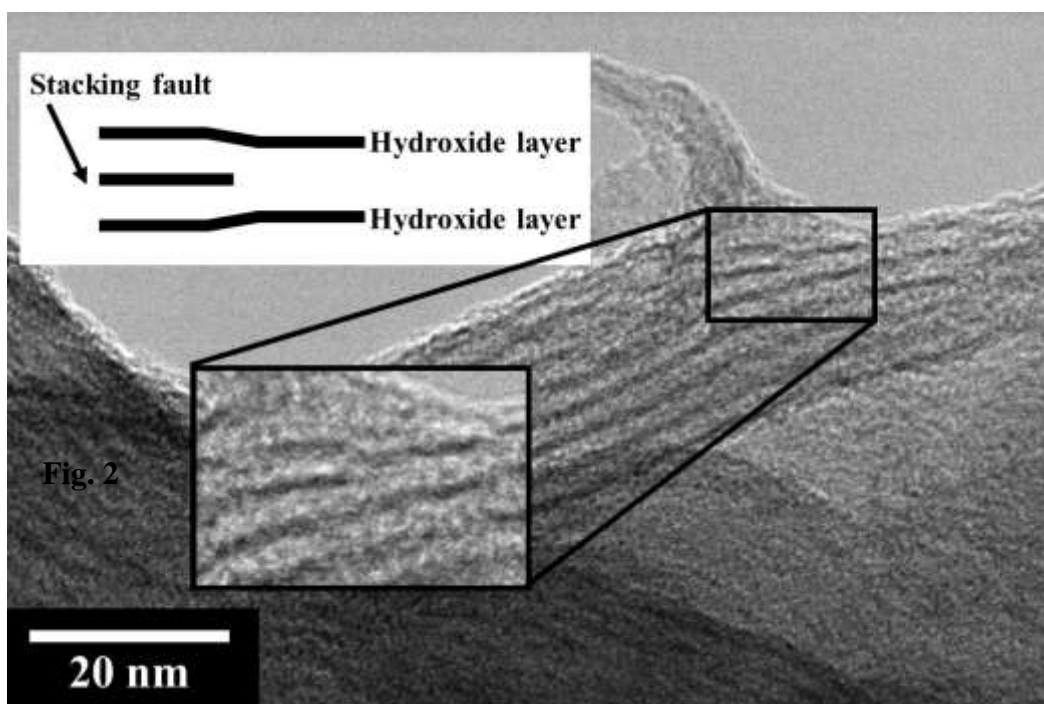
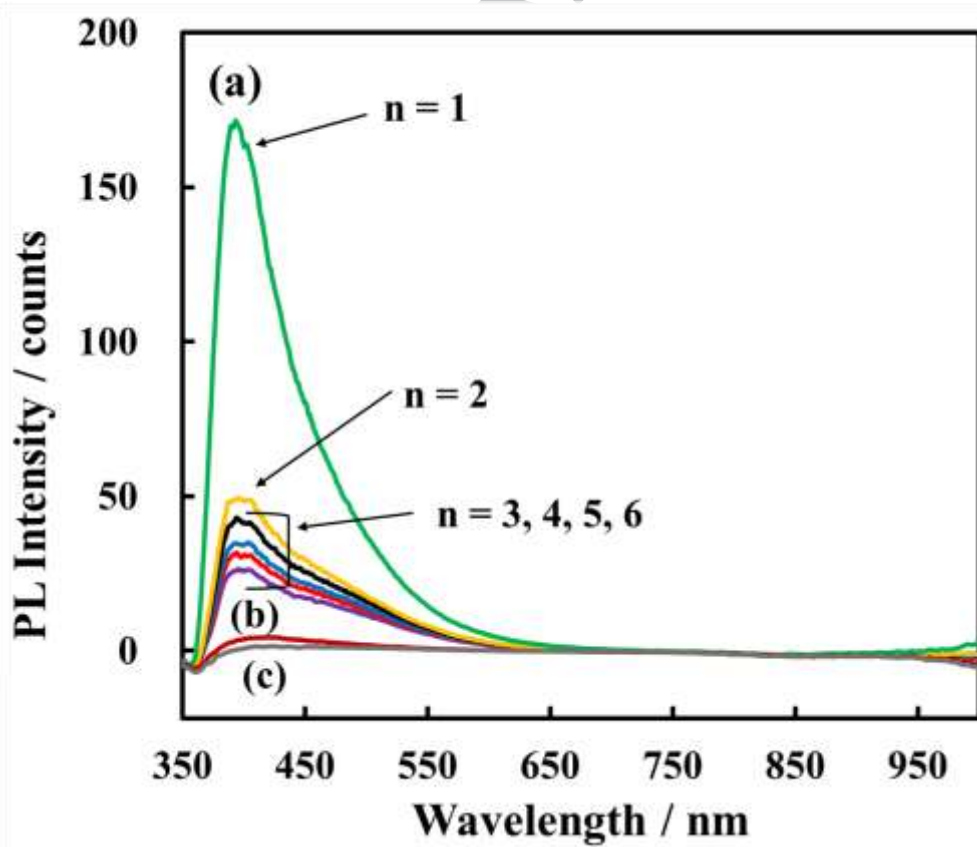


Fig. 1





Highlights

- Stacking faults in LDH were observed by HRTEM.
- LDH with intercalation of laurate ions exhibited photoluminescence.
- Interlayer of LDH was expanded by intercalating laurate ions.

ACCEPTED MANUSCRIPT