

Letter

Morphological control of layered double hydroxide through a biomimetic approach using carboxylic and sulfonic acids


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ABSTRACT

Layered double hydroxides (LDHs) have intercalation properties and are used in various applications. The performances of the LDH materials can be improved by controlling crystal morphology. Morphology of inorganic crystals is controlled by organic molecules in biomineralization. Inspired by biomineralization, we investigated the effect of the addition of mono, di and triacids as morphological control agents on crystal morphology of LDH synthesized by the homogeneous precipitation method. Morphology of LDH was changed from hexagonal plate to stacked disc by addition of monoacids, namely acetic acid and methanesulfonic acid, in the reaction solution. Flower-shaped LDH crystals were formed in the presence of diacids and a triacid, namely succinic acid, 1,2-ethanedisulfonic acid and 1,2,3-propanetricarboxylic acid. We found that the morphology of the LDH crystals was controlled by the number of functional group on the morphological control agent rather than the type of functional group. These findings can contribute for the development of novel and functional LDH materials with precisely controlled morphology.

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1. Introduction

Biomimetic synthesis of inorganic crystals with controlled morphology, including crystal assemblies, has received much attention in the field of materials chemistry [1–3]. Living organisms use soluble organic molecules and insoluble organic templates to precisely control the morphology of inorganic crystals in their hard tissues [4]. Biomineralization-inspired morphological control techniques are regarded as a promising approach to produce novel functional materials.

To date, the synthesis of inorganic crystals with controlled morphology has been focused mainly on common inorganic biominerals, such as calcium carbonates [5,6] and calcium phosphates [7–10]; however, the number of target substances for biomimetic mineralization is currently being expanded beyond common inorganic biominerals [11–13]. Layered double hydroxides (LDHs) form one class of substances that are targeted for morphological control through a biomimetic approach [14,15]. LDHs have layered structures and intercalate various anions in their interlayers [16]. There are many studies that use LDHs for environmental purifications [17], biomedical application [18], and as catalysts [19] by utilizing their intercalation properties. LDHs are generally obtained as hexagonal plate-shaped crystals. The performance of LDH materials may be improved by morphological control of LDH crystals. For instance, for water purification processes, a rapid ion exchange is preferred, and the rate of ion exchange can

be controlled by crystal morphology because the exchange occurs at the prism plane. However, separation of the plate-shaped crystals from purified water by filtration, after adsorption of harmful anions, is hampered by clogging caused by the crystals. This problem may be solved by a morphological change of the LDH from a plate shape to a spherical shape. Establishing a guideline about morphological control contributes for improving properties of LDH materials as well as for the creation of novel LDH materials.

Carboxylic and sulfonic acids are good candidates for morphological control agents (MCAs) of LDH crystals. The effects of glycine on crystal morphology during the homogeneous precipitation of MgAl-LDH, which contains Mg^{2+} and Al^{3+} as its cation components, were previously investigated [15]. The morphology of the MgAl-LDH changed from a hexagonal plate to a disc shape and eventually to a stacked-disc arrangement with increasing glycine concentration. The morphological change was caused by adsorption of glycine molecules on the surface of the LDH crystals. The isoelectric point of MgAl-LDH is around pH 11 [20] and hence the LDH crystals carried a positive charge during their synthesis. The adsorption of the negatively charged carboxy group of glycine on the crystal surface likely had a critical impact on the final morphology of the crystals. Hence, negatively charged functional groups on a MCA, such as carboxylic and sulfonic acids, are expected to play a key role in controlling the LDH crystal shape. Additionally, the number of acidic groups on the MCA molecule can also be important for morphological control. However, effects of the type and number of functional groups of MCAs on the morphology of LDHs are unclear. In the present study, we used acetic acid (AA), succinic acid (SA), 1,2,3-propanetricarboxylic acid (PA), methanesulfonic acid (MA),

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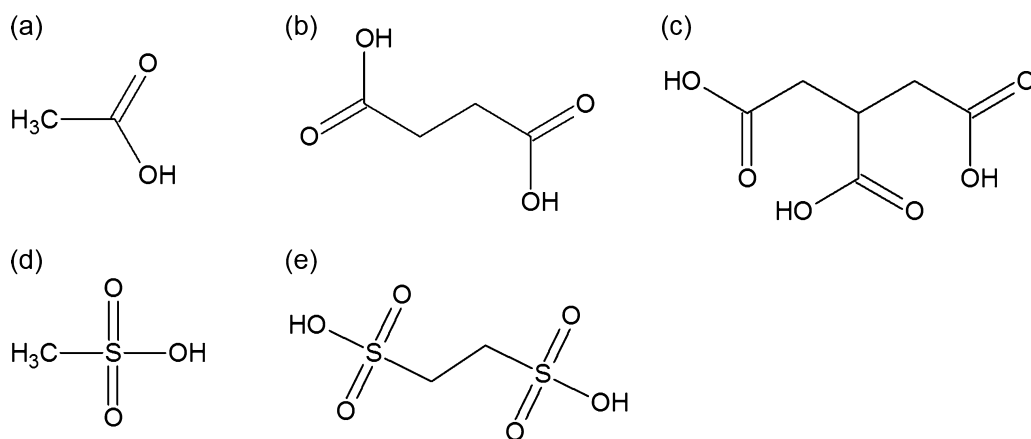


Fig. 1. Chemical structures of organic acids used as morphological control agent. (a) Acetic acid (AA), (b) succinic acid (SA), (c) 1,2,3-propanetricarboxylic acid (PA), (d) methanesulfonic acid (MA), and (e) 1,2-ethanedisulfonic acid (EA).

and 1,2-ethanedisulfonic acid (EA) as MCAs and investigated the effect of these organic acids on the morphology of LDH crystals. The chemical structures of the studied MCAs are shown in Fig. 1.

2. Experimental procedures

2.1. Chemicals

1,2,3-Propanetricarboxylic acid (PA, $\text{HOOCCH}_2\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$, 98.0%) and 1,2-ethanedisulfonic acid dihydrate (EA, $\text{HO}_3\text{SCH}_2\text{CH}_2\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$, 95.0%) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. The following reagents were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan: magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 99.0%), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 98.0%), urea (H_2NCONH_2 , 99.0%), acetic acid (AA, CH_3COOH , 99.7%), succinic acid (SA, $\text{HOOCCH}_2\text{CH}_2\text{COOH}$, 99.5%), methanesulfonic acid (MA, $\text{CH}_3\text{SO}_3\text{H}$, 98.0%), sodium hydroxide (NaOH, 97.0%), nitric acid (HNO_3 , 60–61%), and sodium hydrogen carbonate (NaHCO_3 , 99.5–100.3%). These chemicals were used without further purification.

2.2. Synthesis and characterization of samples

We prepared aqueous solutions with a pH of 3.0 containing 100 mol m^{-3} magnesium nitrate, 50 mol m^{-3} aluminum nitrate, 300 mol m^{-3} urea, and a single morphological control agent (AA, MA, SA, EA or PA). The concentrations of the monoacids AA and MA were 100 mol m^{-3} , the concentrations of the diacids SA and EA were 50 mol m^{-3} and the concentration of the triacid PA was 33.3 mol m^{-3} , resulting in an overall concentration of 100 mol m^{-3} for the carboxy or sulfo group. The pH of the solution was adjusted with sodium hydroxide. A solution with a pH of 3.0 containing 100 mol m^{-3} magnesium nitrate, 50 mol m^{-3} aluminum nitrate, and 300 mol m^{-3} urea was also prepared. The pH of this solution was adjusted with nitric acid. Fifty cm^3 aliquots of the prepared solutions were maintained at 90°C for 5 days to form the LDHs. The pH values of the solutions after the reaction were measured by glass-electrode type pH meter (Horiba, 9625-10D, Kyoto, Japan) at solution temperatures of approximately 25°C . The formed precipitates were collected by vacuum filtration and dried at 90°C for overnight.

Crystal phase and crystal morphology were characterized by powder X-ray diffraction (XRD, RINT-2200VL, Rigaku Co., Tokyo, Japan) and scanning electron microscope (SEM, SU-8000, Hitachi, Ltd., Tokyo, Japan) after thin platinum film coating, respectively.

Additionally, we examined the crystalline phases by XRD of samples after exchange of interlayer anions by carbonate ions. To this end, 50 mg samples were suspended in 50 cm^3 of a 100 mol m^{-3} sodium hydrogen carbonate solution. After 3 h, the samples were collected and dried overnight at 90°C .

The samples synthesized with AA, SA, PA, MA, and EA were labeled as AA-LDH, SA-LDH, PA-LDH, MA-LDH, and EA-LDH, respectively. The LDH synthesized in the absence of a MCA is denoted as CONTROL.

3. Results and discussion

All the solutions had an initial pH of 3.0. The pH values of CONTROL, AA-LDH, SA-LDH, PA-LDH, MA-LDH, and EA-LDH after the reaction were 8.0, 8.0, 8.1, 8.0, 8.1, and 8.1, respectively. The pH of the solutions had increased because of ammonia formation through urea hydrolysis. The final pH values of the reaction solutions were independent of the type of MCA.

Fig. 2 shows the powder XRD patterns of the isolated solids. Based on the powder diffraction file # 01-089-0460 ($\text{Mg}_{0.667}\text{Al}_{0.333}(\text{OH})_2(\text{CO}_3)_{0.167}(\text{H}_2\text{O})_{0.5}$), the characteristic LDH

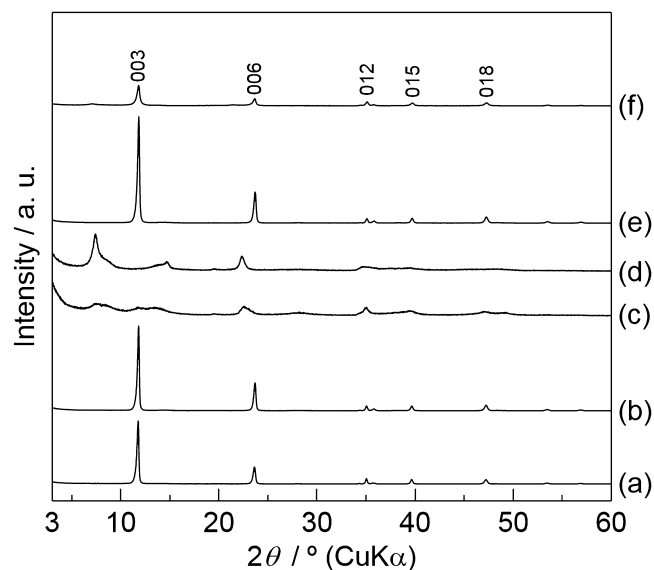


Fig. 2. Powder X-ray diffraction patterns of as-prepared samples: (a) CONTROL, (b) AA-LDH, (c) SA-LDH, (d) PA-LDH, (e) MA-LDH, and (f) EA-LDH. Reflection peak intensities of SA-LDH and PA-LDH are increased five times.

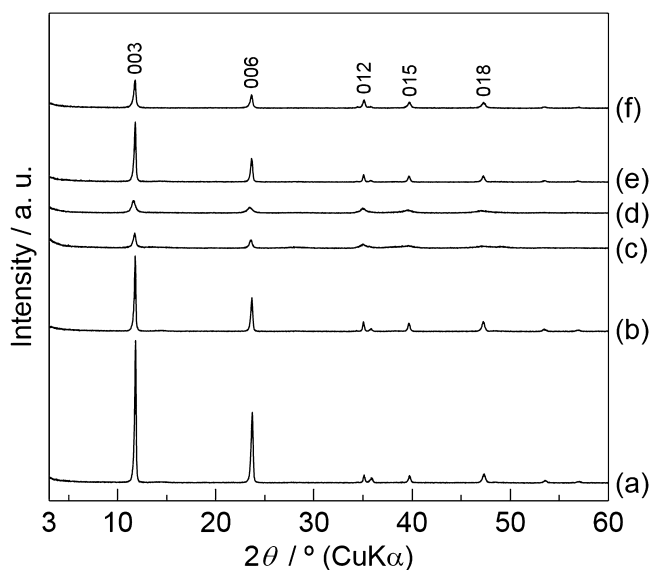


Fig. 3. Powder X-ray diffraction patterns of samples treated with sodium hydrogen carbonate solution: (a) CONTROL, (b) AA-LDH, (c) SA-LDH, (d) PA-LDH, (e) MA-LDH, and (f) EA-LDH.

reflection peaks of 003, 006, 012, 015, and 018 were detected in CONTROL, AA-LDH, MA-LDH, and EA-LDH. Broad reflection peaks were detected in SA-LDH and PA-LDH.

The powder XRD patterns of samples treated with sodium hydrogen carbonate solution are provided in Fig. 3. After this treatment, the LDH phase was detected in all samples, including SA-LDH and PA-LDH. Most likely, SA and PA-intercalated LDHs were formed initially, and SA and PA were exchanged by carbonate ions during treatment with sodium hydrogen carbonate solution. The order of full width at half-maximum (FWHM) values of 003 reflection peak of samples was CONTROL < AA-LDH < MA-LDH < EA-LDH < SA-LDH < PA-LDH. SA-LDH and PA-LDH had relatively larger FWHM values. Hence the crystallinities of the LDH formed in the SA-LDH and PA-LDH were lower than the other samples. Very broad and weak reflection peaks derived from γ -AlOOH (PDF: # 01-074-1895)

were also detected for SA-LDH and PA-LDH, although the reflection peaks were hardly observed in Fig. 3 due to its low intensity.

The morphology of as-prepared samples is shown in Fig. 4. Hexagonal plate-shaped precipitates were observed in the CONTROL. According to Figs. 2 and 3, the plate-shaped precipitates were LDH crystals. Stacked-disc-shaped precipitates were observed in the AA-LDH and MA-LDH. The crystal size of stacked-disc-shaped precipitates observed in the AA-LDH was larger than that in the MA-LDH. These stacked-disc-shaped precipitates were LDH crystals based on the XRD analysis (Figs. 2 and 3). These results imply that the AA slightly inhibits nucleation of LDH, resulting in larger LDH formation because the amounts of ions, such as Mg^{2+} , Al^{3+} , CO_3^{2-} and OH^- , supplied for one LDH nucleus were increased. Flower-shaped precipitates were observed in the PA-LDH and EA-LDH. Flower-shaped and tiny irregular-shaped precipitates were observed in SA-LDH. According to Figs. 2 and 3, flower-shaped precipitates were LDH crystals and the irregular-shaped precipitates observed in SA-LDH might be low-crystalline LDH and/or γ -AlOOH.

SA-LDH intercalated SA and PA-LDH intercalated PA, while EA-LDH did not intercalate EA (Figs. 2 and 3). However, flower-shaped crystals were formed in these samples (Fig. 4). These results imply that intercalation of organic molecules does not affect the morphology of LDH crystals.

The crystal morphology observed in AA-LDH was similar to that observed in MA-LDH (Fig. 4). Additionally, the crystal morphology observed in SA-LDH was similar to that observed in EA-LDH (Fig. 4). As shown in Fig. 1, AA and MA have one carboxy and one sulfo group, respectively. SA and EA have two carboxy and two sulfo groups, respectively. Our findings suggest that the morphology of LDH is controlled by the number of functional groups in the MCA, rather than the type of functional group. The crystal morphology observed in PA-LDH was similar to that observed in SA-LDH and EA-LDH (Fig. 4). These results imply that organic acids having two or more negatively charged functional groups contribute to the formation of flower-shaped LDH crystals.

Stacked-disc-shaped crystals were formed in the case of AA-LDH and MA-LDH and this crystal morphology is similar to the LDH synthesized in the presence of glycine [15]. This implies that the morphological change mechanism of LDH induced by AA and MA was the same as that induced by glycine. Therefore, the morphological change most likely occurred by adsorption of AA or MA on the

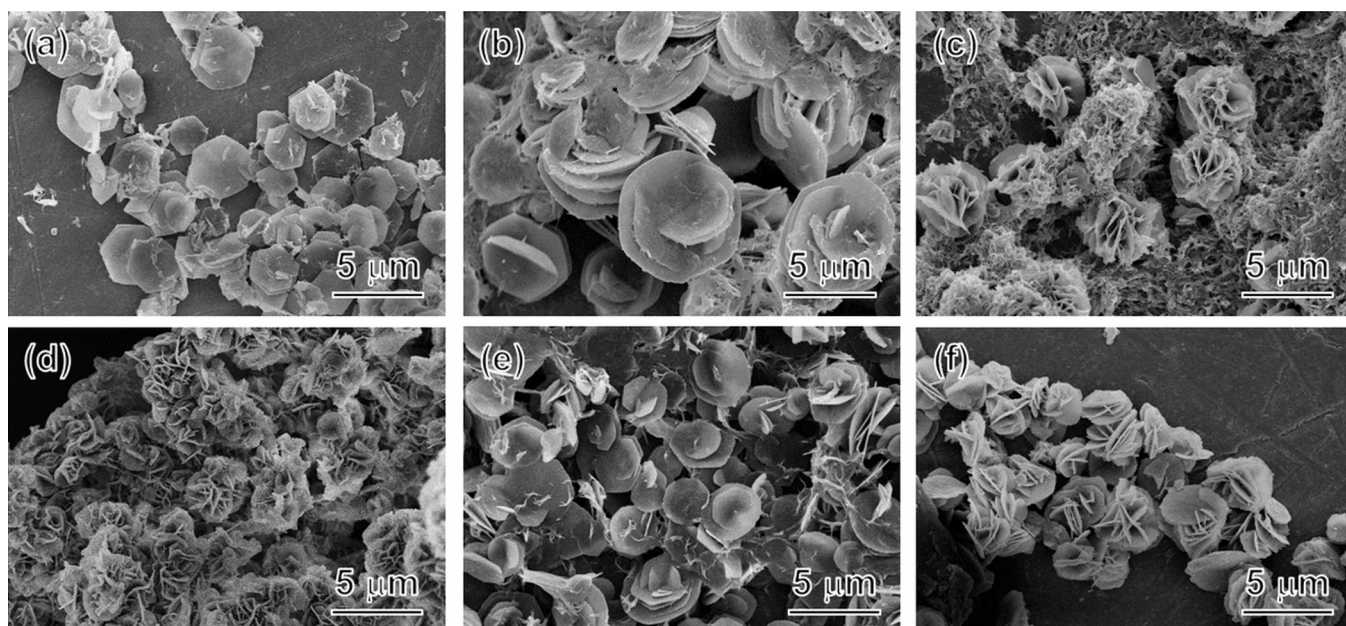


Fig. 4. Scanning electron microscopic images of as-prepared samples: (a) CONTROL, (b) AA-LDH, (c) SA-LDH, (d) PA-LDH, (e) MA-LDH, and (f) EA-LDH.

basal plane of LDH during crystal growth. Adsorbed AA or MA likely inhibited bonding between the substrate and the newly formed LDH crystals resulting in the formation of stacked-disc-shaped LDH crystals.

Flower-shaped crystals were formed in the case of SA-LDH, PA-LDH and EA-LDH. Formation of flower-shaped LDH crystals was reported previously by Okamoto et al. [21]. In their report, the LDH synthesized by the homogeneous precipitation method was changed from hexagonal plate shape to flower shape with increasing amounts of hexamethylenetetramine in the reaction solution. Hexamethylenetetramine was used to increase solution pH for the homogeneous precipitation. The strategy of their morphological control technique was quite different from our strategy. Hence synthetic method of flower-shaped LDH crystals using organic acids can be regarded as a novel technique. Three possible scenarios may explain the formation of flower-shaped crystals. Flower-shaped crystals were specifically formed in the presence of MCAs with two or more negatively charged functional groups. This implies that the number of functional groups on the MCA is an important factor for the formation of flower-shaped crystals. First, we discuss the formation of flower-shaped crystals based on the classical crystal growth theory. According to this theory, crystal morphology is changed far from equilibrium with increasing degree of supersaturation [22]. The crystals formed in the CONTROL possess a polyhedral shape. Hence, the hexagonal plate-shaped crystals were likely formed under conditions of low supersaturation. Flower-shaped crystals are formed from radially growing nuclei. This type of polycrystals are formed under conditions of high supersaturation. Hence, SA, PA and EA inhibited nucleation of the LDH by interacting with the embryos. Nucleation and crystal growth during LDH formation with SA, PA and EA occurred under conditions of higher supersaturation than with other reaction systems. As a result, flower-shaped crystals were formed. Next, we discuss morphology formation based on crystal growth theory and taking into account the concept of heterogeneous nucleation. During LDH formation, the pH of the reaction solution was weakly alkaline. Under these conditions, SA, PA and EA are deprotonated and have a negative charge. After nucleation of the LDH crystals, the negatively charged SA, PA and EA molecules adsorbed on the LDH nanocrystals through electrostatic interaction. The adsorbed SA, PA and EA molecules may have a free functional group, which is not used for adsorption of these organic acids on the LDH crystal surface. The free functional group likely induced heterogeneous nucleation on the LDH nanocrystals and this resulted in the formation of nano-sized LDH polycrystals. Subsequently, the crystals continued to grow in a radial fashion to form a flower-shaped LDH. Finally, we discuss here the formation of the flower-shaped crystals through self-assembly. After nucleation, the negatively charged SA, PA and EA molecules adsorbed on the LDH nanocrystals through electrostatic interaction, thereby decreasing the electrostatic repulsion between the LDH nanocrystals. Assemblies of nanocrystals continued to grow in a radial fashion to form flower-shaped crystals.

Future studies should provide a detailed explanation of the mechanism of formation of flower-shaped LDH crystals. However, this work demonstrates that the morphology of LDH crystals can be controlled by the number of negatively charged functional groups on one MCA molecule rather than the type of functional group. We expect that the obtained flower-shaped LDH crystals are less likely than plate-shaped crystals to clog the pores during filtration. The morphological control technique inspired by biomineralization can be applied for the synthesis of LDHs for water purification.

4. Conclusions

We investigated the effect of the addition of mono and diacids as MCAs on crystal morphology of a LDH synthesized by the

homogeneous precipitation method. Hexagonal plate-shaped LDH crystals were formed in the absence of a MCA. Stacked-disc-shaped LDH crystals were formed in the presence of the monoacids AA and MA. Flower-shaped LDH crystals were formed in the presence of diacids SA and EA and triacid PA. These findings indicated that the morphological control technique inspired by biomineralization is effective for LDHs. Additionally, it is noteworthy that the morphology of the LDH crystals was controlled by the number of functional group on the control agent rather than the type of functional group. Our findings can be a guideline of the morphological control of LDH crystals and contribute for the development of novel and functional LDH materials.

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References

- [1] Y. Han, T. Nishimura and T. Kato, *Polym. J.*, 46, 499–504 (2014).
- [2] R.-H. Jin, D.-D. Yao and R.T. Levi, *Chem. Eur. J.*, 20, 7196–7214 (2014).
- [3] A. Arakaki, K. Shimizu, M. Oda, T. Sakamoto, T. Nishimura and T. Kato, *Org. Biomol. Chem.*, 13, 974–989 (2015).
- [4] S. Mann, *Biomineralization Principles and Concepts in Bioinorganic Materials Chemistry*, Oxford University Press, Oxford (2001).
- [5] H. Imai, T. Terada and S. Yamabi, *Chem. Commun.*, 484–485 (2003).
- [6] T. Nishimura, H. Imai, Y. Oaki, T. Sakamoto and T. Kato, *Chem. Lett.*, 40, 458–460 (2011).
- [7] Y. Zhang and J. Lu, *Cryst. Growth Des.*, 8, 2101–2107 (2008).
- [8] T. Yokoi, M. Kawashita, K. Kikuta and C. Ohtsuki, *Mater. Sci. Eng. C*, 30, 154–159 (2010).
- [9] T. Nonoyama, M. Tanaka, T. Kinoshita, F. Nagata, K. Sato and K. Kato, *Chem. Commun.*, 46, 6983–6985 (2010).
- [10] T. Yokoi, M. Kawashita and C. Ohtsuki, *J. Cryst. Growth*, 383, 166–171 (2013).
- [11] T. Nonoyama, T. Kinoshita, M. Higuchi, K. Nagata, M. Tanaka, K. Sato and K. Kato, *J. Am. Chem. Soc.*, 134, 8841–8847 (2012).
- [12] K. Tomizaki, S. Kubo, S.-A. Ahn, M. Satake and T. Imai, *Langmuir*, 28, 13459–13466 (2012).
- [13] Z. Tong, Y. Jiang, D. Yang, J. Shi, S. Zhang, C. Liu and Z. Jiang, *RSC Adv.*, 4, 12388–12403 (2014).
- [14] B. Li, J. He, D.G. Evans and X. Duan, *J. Phys. Chem. Solids*, 67, 1067–1070 (2006).
- [15] T. Yokoi and M. Kamitakahara, *Chem. Lett.*, 43, 234–236 (2014).
- [16] A.I. Khan and D. O'Hare, *J. Mater. Chem.*, 12, 3191–3198 (2002).
- [17] K.-H. Goh, T.-T. Lim and Z. Dong, *Water Res.*, 42, 1343–1368 (2008).
- [18] K. Ladewig, A.P. Xu and G.Q. Lu, *Expert Opin. Drug Deliv.*, 6, 907–922 (2009).
- [19] S. Omwoma, W. Chen, R. Tsunashima and Y.-F. Song, *Coord. Chem. Rev.*, 258–259, 58–71 (2014).
- [20] Y. Li, W.-G. Hou and W.-Q. Zhu, *Colloids Surf. A*, 303, 166–172 (2007).
- [21] K. Okamoto, N. Iyi and T. Sasaki, *Appl. Clay Sci.*, 37, 23–31 (2007).
- [22] I. Sunagawa, *Crystals: Growth, Morphology, & Perfection*, Cambridge University Press, Cambridge (2005).

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