Preparation of layered double hydroxide coating films via the aqueous solution process using binary oxide gel films as precursor

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Layered double hydroxides (LDHs) are inorganic materials consisting of the hydroxide layers formed with at least two metallic elements and anions between the layers. In this study, we have investigated the functionalization of LDH coating films by modification of both sol–gel and aqueous solution processes. A binary oxide system, Al_2O_3–TiO_2, was used for the precursor gel films. Judging from XRD and SEM measurements, LDH crystals were generated for the wide range of gel composition. Therefore, coating films with composite structure of Zn–Al LDH and TiO_2 was obtained by simple process. The reconstruction of LDH, i.e., heat treatment and following incubation in aqueous solution, was also achieved. This process can be expected for the intercalation of functional molecules in LDH layers and crystallization of TiO_2 for these composite coatings.

Key-words : Layered double hydroxide, Sol–gel method, Aqueous solution process, Crystal growth, Composite coating

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1. Introduction

Studies on layered double hydroxides (LDHs), known as hydrotalcite-like anionic clays materials, have been conducted over the past several decades since they have many possibilities of the applications for anion exchangers, catalysts, and the immobilization hosts of functional molecules by intercalation into their layers.[1)–6)] LDHs consist of positively charged brucite-like layers, where a fraction of the divalent cations is replaced by trivalent cations. The positively-charged layers are separated by the charge-balancing anions and water molecules.[7)] Up to the present time, most of studies on LDHs were focused on powder samples prepared through the co-precipitation process.[2),8)] For the application of optical and electronic devices, coating films of LDH on the substrates should be suitable. Unlike many other layered materials, however, LDHs are notoriously difficult to fabricate into coating films. A variety of attempts to prepare LDH films have been previously reported in the literature.[1),9)–11)] Simplest approach is coating of LDH powders using organic binders. However, the existence of binders should be hard on the applications, especially for the electronic devices. Development of the binder-free synthetic process of LDH coatings is expected for the next generation of LDH applications. Recently, Yamaguchi and co-workers have succeeded in the direct immobilization of Zn–Al LDH on substrates by treating Al_2O_3–ZnO amorphous thin films with hot water.[12)] We have also reported that a hydrotalcite-like film has been successfully deposited on an Al-bearing glass substrate based on an interface reaction between an Al (metal) layer and a zinc aqueous solution.[13)] The film selectively grew on the Al surface but not on the bare glass surface. However, some limitation existed in this method due to the preparation process of precursor Al layer. On the other hand, direct formation of LDHs has been reported to be possible on Al_2O_3 surfaces using aqueous solutions of Co^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, etc.[14)–17)] Paulhiac and Clause reported the surface precipitation of Co^{2+}, Ni^{2+}, or Zn^{2+} with Al^{3+} during impregnation of alumina at neutral pH.[14)] It is well known that Al_2O_3 coating films were easily prepared on various types of substrates by the sol–gel method.[18)–20)] Under these backgrounds, we have recently reported that the sol–gel derived Al_2O_3 coating films can be transformed to LDH via reaction with aqueous solution of M^{2+} ions.[21)] However, the size of LDH crystals formed in these systems is large enough to cause scattering in the visible light region, and the LDH films is almost opaque. In present paper, a binary oxide system, Al_2O_3–TiO_2, was employed for the precursor gel films. TiO_2 content was hard to convert into LDH. Therefore, control of the composition of precursor gel films should give transparent LDH films, which is favorable to evaluate optical properties of LDH coatings. Moreover, coating films with composite structure with LDH and TiO_2 should be obtained in this system. This composite system can be expected for the platform of hybrid devices based on the combination of the host property of LDHs and the photoactivity of TiO_2. The effects of the composition of Al_2O_3–TiO_2 on the LDH formation by the reaction with aqueous solutions of zinc acetate were investigated in detail.

2. Experimental procedure

Aluminum tri-*sec*-butoxide (Al–(O–*sec*–Bu)$_3$), titanium tetrabutoxide (Ti(O–*n*C_4H_9)$_4$), and zinc acetate were obtained from Wako Pure Chemical Industries, Ltd. Ethylacetoacetate (EAcAc), 2-propanol (*i*–PrOH), acetic acid, and ammonia water (28%) were purchased from Kishida Chemical Co., Ltd. All reagents were used as received without any further purification. The water used in all experiments was deionized by a Milli–Q system (Direct–Q, Millipore Corporation). Glass substrates used for substrates were cleaned by using the RCA protocol (i.e., by immersing in a 5:1:1 H_2O/30% H_2O_2 aq./28% NH_4OH aq. (v/v/v) mixture for 10 min at 70°C), followed by rinsing with the deion-

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ized water.

Al_2O_3–TiO_2 gel films were prepared from Al–(O–*sec*–Bu)$_3$, Ti(O–*n*C_4H_9)$_4$ according to the following procedure. Al–(O–*sec*–Bu)$_3$, EAcAc and *i*-PrOH were mixed and stirring at room temperature for 1 h. A mixture of Ti(O–*n*C_4H_9)$_4$ and ethanol was added to the solution and the resultant mixture was stirring at room temperature for 1 h. Then a mixture of water and *i*-PrOH was then added dropwise to the solution for hydrolysis and the solution was stirring for 1 h. Molar ratios of Ti versus Al were chosen to be 0:1, 1:5, 1:1 and 5:1. Coating was carried out on glass substrate by dipping with a withdrawing speed of 3 mm/s. The obtained Al_2O_3–TiO_2 gel films were then immersed in aqueous solutions of zinc acetate (1.5×10^{-2} mol dm^{-3}) at 97°C for 10 min and dried overnight at 50°C.

The reconstruction of LDH was carried out by heat-treatment of the films at 400°C for 30 min, and subsequent immersion of the films in distilled water at room temperature for 30 min.

Surface morphology of coated films was examined by scanning electron microscopy (SEM; Hitachi, Ltd., S–3000N). X-ray diffraction (XRD) patterns were recorded with a Rigaku Co., RINT2100 X-ray diffractometer with Cu Kα radiation. Optical transmission spectra were measured by a JASCO Co., V–570 UV-visible spectrophotometer.

3. Results and discussion

Formation of LDH can be confirmed by XRD measurements. Before the immersion in zinc acetate solutions, the Al_2O_3–TiO_2 gel films were amorphous. On the other hand, two typical peaks were observed after immersion in a zinc acetate aqueous solution at 97°C for 10 min. **Figure 1** shows the XRD patterns of the Al_2O_3–TiO_2 gel films with various Al/Ti ratios, immersed in a zinc acetate aqueous solution. The peaks were observed at 12° and 23°, which could be assigned to (003) and (006) reflections of LDH crystals with intercalated carbonate anions, respectively. It agrees well with the published values for Zn–Al LDH.[5)] The intensity of the peaks changes with the ratio of Al and Ti of the original gel films. Interestingly, the strongest diffraction peaks were observed in the case of the gel film with the atomic ratio Al/Ti unity.

Surface morphology of Al_2O_3–TiO_2 gel films after immersion in a zinc acetate aqueous solution for 10 min was shown in **Fig. 2**. Morphological difference of the surface of coating films after immersion was found with the composition of the film. The gel films with Al/Ti ratio of 1:0 (a) and 5:1 (b) show reticulation structure after immersion in zinc acetate solutions. It seems that LDH crystals stand perpendicularly on the substrate. On the other hand, the surface morphology of the films with Al/Ti ratio of 1:1 (c) and 1:5 (d) is different from that of the films with Al/Ti ratio of 1:0 (a) and 5:1 (b). The amount of formed LDH after treatment with zinc acetate solution was small and the LDH crystals deposit parallel to the substrates. These results well-correspond to the results of XRD measurements. In the case of the gel films with Al/Ti ratio of 1:0 and 5:1, no peaks were found in XRD pattern. It is due to the orientation of LDH crystals on the substrate, and does not indicate that LDHs are not formed in these conditions. The formation of LDHs from gel films consists with dissolution-reprecipitation process. Therefore, the formation rate of LDHs should depend on the dissolution rate of Al ions from gel films. We have reported that the crystalline growth behavior of LDH from Al_2O_3 gel films by the aqueous solution process.[21)] LDH crystals deposit parallel to the substrates at the initial stage of reaction and it changes to be oriented perpendicular to the substrate with increasing reaction time. Here, Al ion dissolution was fast in the case of gel films with a large portion of Al_2O_3. Therefore, the reaction completed within 10 min. On the other hand, the dissolution rate of Al ions was much slower in the case of gel film with high TiO_2 ratio, and thus LDH crystals deposited parallel to the substrates after the reaction for 10 min.

These results indicate that the transparency of LDH coatings depends on the composition of gel films. The deposition amount, the deposition rate, and the deposition morphology are influenced by the Al/Ti composition and cause difference in the transparency of LDH films. **Figure 3** shows the optical transmission spectra of Al_2O_3–TiO_2 gel films immersed in a zinc acetate aqueous solution. The ratios of Al and Ti in the gel films were 1:0, 1:5, 1:1 and 5:1. The transmission spectrum of glass substrate without coating is also shown for comparison. The transmittance of the coated substrate decreases with an increase in the ratio of Al because of light scattering by LDH crystals formed on the gel films. It is noteworthy that the transparency of the coating films was improved with increase of the TiO_2 contents. When $85TiO_2 \cdot 15AlO_{3/2}$ gel films was employed as precursor the optical transmittance of LDH coating films is higher than 80% in the

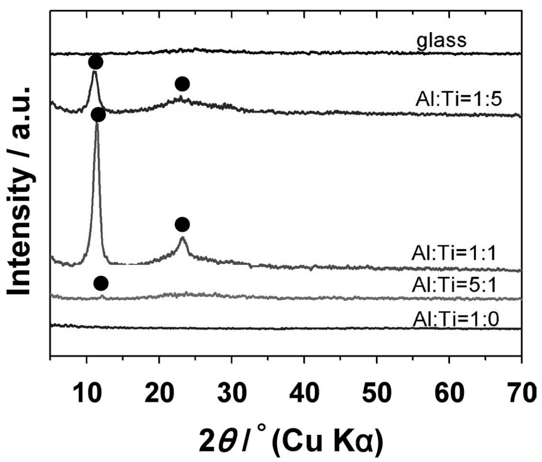

Fig. 1. XRD patterns of Al_2O_3–TiO_2 gel films immersed in a zinc acetate aqueous solution. The ratios of Al and Ti in the gel films were 1:0, 1:5, 1:1 and 5:1. Closed circle symbols indicate reflection peaks of LDH crystal with intercalated carbonate anions.

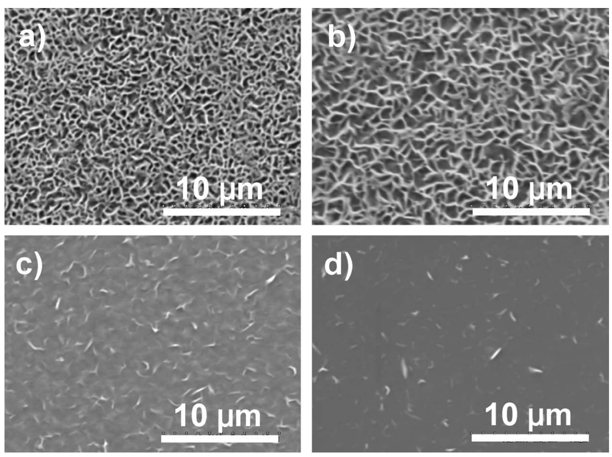

Fig. 2. SEM micrographs of surface of Al_2O_3–TiO_2 gel films immersed in a zinc acetate aqueous solution. The ratios of Al and Ti in the gel films were (a) 1:0, (b) 5:1, (c) 1:1 and (d) 1:5.

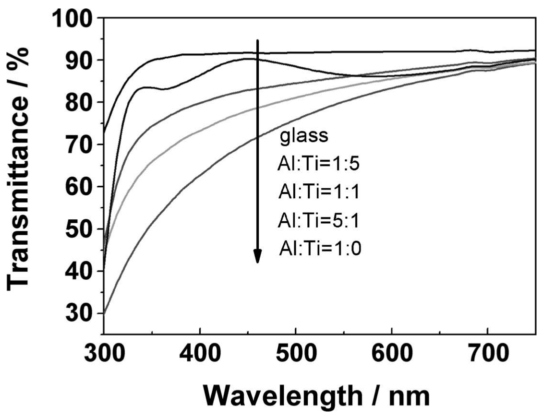

Fig. 3. Optical transmission spectra of Al_2O_3–TiO_2 gel films immersed in a zinc acetate aqueous solution. The ratios of Al and Ti in the gel films were 1:0, 1:5, 1:1 and 5:1.

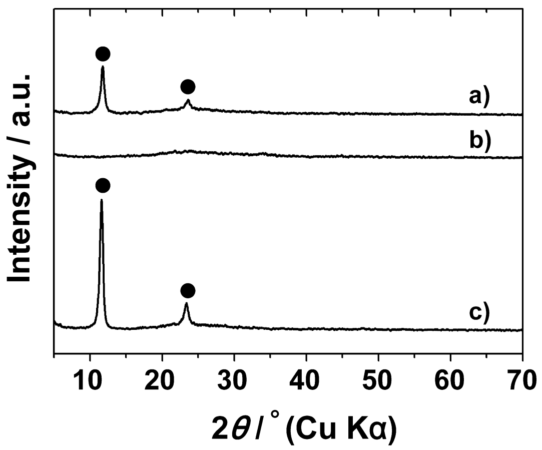

Fig. 4. XRD patterns of LDH films formed from Al_2O_3–TiO_2 gel films; (a) before reconstruction process, (b) after heat-treatment at 400°C, (c) after heat-treatment at 400°C and subsequent immersion in distilled water. The ratio of Al and Ti in the gel film was fixed to 1:1. Closed circle symbols indicate reflection peaks of LDH crystal with intercalated carbonate anions.

visible range. Thus, almost transparent LDH coatings were achieved in this composition.

XRD patterns of LDH coating films after reconstruction process were shown in **Fig. 4**. The molar ratio of Al and Ti in the gel film was fixed to 1:1. When the film was heated at 400°C, the typical peaks assigned to LDH crystals were disappeared. It indicates that the LDH crystals decomposed by elimination of the interlamellar anions. After the immersion in the distilled water, the peaks restored. It indicates that the LDH crystals were reconstructed by rehydration. In this system, LDH should be formed as the Zn–Al type and the major component of residual base films after aqueous solution reaction should consist mainly of TiO_2 since TiO_2 content is hard to convert into LDHs. Therefore, the composite structure with Zn–Al LDH and TiO_2 was obtained by simple process. The residual TiO_2 in the base films should be in the amorphous state after the aqueous solution reaction. The reconstruction process, heat-treatment and following incubation in aqueous solution, can achieve the intercalation of functional molecules in LDH layers, as well as the crystallization of TiO_2 for these composite coatings. This composite system can be expected for the platform of hybrid devices based on the combination of the host property of LDHs and the photoactivity of TiO_2.

4. Conclusions

LDH coating on the substrates has been achieved by aqueous solution treatment of sol–gel derived Al_2O_3–TiO_2 gel films with various Al/Ti ratios. Zn–Al LDHs were successfully deposited on the gel films by immersion of gel films into the zinc acetate solution. The transparency of LDH coatings is controllable by changing the ratio of Al/Ti of precursor gel films. In the case of $85TiO_2 \cdot 15AlO_{3/2}$ film, the optical transmittance of obtained LDH coating films was higher than 80% in the visible range. When the obtained LDH film was heated at 400°C, the LDH crystals decomposed. After the immersion in the distilled water, the LDH crystals were reconstructed by rehydration. Therefore, the composite structure with Zn–Al LDH and TiO_2 was obtained by simple process. Direct formation of the composite structure with Zn–Al LDH and TiO_2 will expand the application fields of LDH.

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