Electrochemical Synthesis of Zn-Al-based Layered Double Hydroxides Intercalated with 4-hydroxy-3-methoxy Cinnamic Acid as a UV-ray Absorbent

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Abstract
One-step electrochemical synthesis of Zn-Al-based layered double hydroxides intercalated with 4-hydroxy-3-methoxy cinnamic acid as a UV-ray absorbent (Zn-Al/HMCA LDH) was attempted in this study. Among various preparation conditions, it was confirmed that HMCA was intercalated into the interlayers of Zn-Al-based layered double hydroxide (Zn-Al LDH) by potentiometric electrolysis at -1.5 V for 1 h at RT. The Zn-Al/HMCA LDH films prepared on a Pt plate showed an excellent UV-ray absorption property.
Keywords: Layered double hydroxide, intercalation, 4-hydroxy-3-methoxy cinnamic acid, UV-ray absorbent

Introduction

Layered double hydroxides (LDH) are very promising in various fields such as catalysis, ion exchange and drug delivery systems [1]. Among them, Zn-Al LDH has received recently considerable attentions, because various functional organic molecules can be intercalated into the interlayers. Generally, LDH is prepared by co-precipitation with constituent metal salts in an aqueous solution. However, it is very difficult to synthesize Zn-Al LDH intercalated with functional organic molecules directly by such a chemical method. On the other hand, electrochemical synthesis may allow us one-step synthesis and compositional control of Zn-Al LDH intercalated with functional organic molecules. Therefore, electrochemical synthesis of Zn-Al/HMCA LDH films on a Pt working electrode has been attempted in this study.

Experimental

Zn-Al/HMCA LDH films were electrochemically prepared on the surface of the Pt electrode (area: 1×1 cm^2) masked by masking tape as follows. After $Al(NO_3)_3{\cdot}9H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were dissolved in deionized water (Al^{3+}: 14.8 mM, Mg^{2+}: 7.4 mM), the solution was mixed with a 44.4 mM HMCA ethanol solution. The Zn-Al/HMCA LDH film was obtained by potentiostatic electrolysis at -1.5~-0.4 V for 1 h in the above mixed solution at RT, using a Pt counter electrode and a saturated Ag/AgCl reference electrode. As a reference, a LDH film without HMCA (Zn-Al LDH) was also prepared in a solution without HMCA. Crystalline structures of the samples obtained were analyzed by XRD, intercalation behavior of HMCA in the Zn-Al/HMCA LDHs was estimated by FT-IR, and their optical properties were measured by UV-VIS diffuse reflectance spectroscopy.

Results and Discussion

Figure 1 shows XRD patterns of Zn-Al LDH and Zn-Al/HMCA LDH films, which were prepared on a Pt electrode by electrolysis at -1.2 V and -1.5 V, respectively. The Zn-Al LDH had a developed layer structure with a basal spacing (d_{003}) of ca. 0.86 nm, which corresponded to the sum of the thickness of ionic NO_3^- (0.38 nm) and that of a brucite-like layer (0.48 nm) [1]. On the other hand, d_{003} of Zn-Al/HMCA LDH was ca. 1.64 nm and thus the interlayer distance is ca. 1.16 nm, which is similar to the molecular length of HMCA. Figure 2 shows a FT-IR spectrum of Zn-Al LDH/HMCA. The spectrum was characterized with asymmetric and symmetric stretching vibrations of carboxyl group at 1511 and 1429 cm^{-1}, respectively, along with O-H stretching of hydroxyl group and deformation vibration of H_2O at 3330 and 1637 cm^{-1}, respectively. From these results, HMCA was suggested to be intercalated into the interlayer spaces of Zn-Al LDH.

UV-VIS diffuse reflectance spectra of Zn-Al LDH and Zn-Al/HMCA LDH are shown in Fig. 3. Zn-Al LDH could hardly absorb UV ray in the range of 250~400 nm. In contrast, Zn-Al/HMCA LDH showed an excellent UV-ray shielding ability, suggesting that HMCA was successfully fixed in the interlayer spaces of Zn-Al LDH.

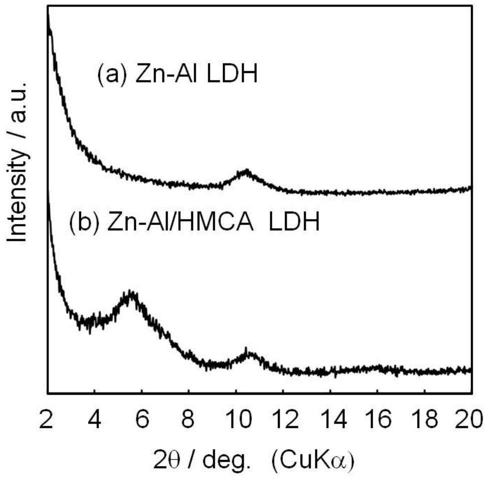

Fig. 1 XRD patterns of LDH thin films; (a) Zn-Al LDH prepared at -1.2 V and (b) Zn-Al/HMCA LDH prepared at -1.5 V.

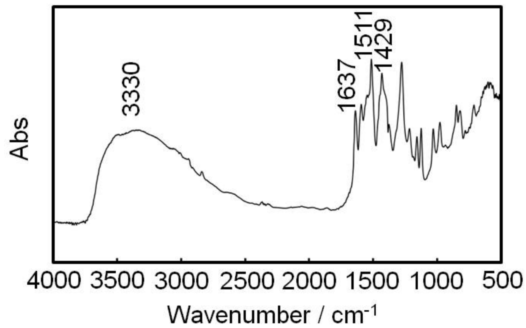

Fig. 2 FT-IR spectrum of a Zn-Al/HMCA LDH film.

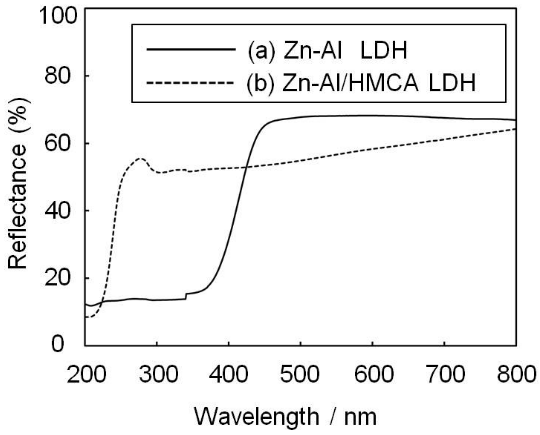

Fig. 3 UV-VIS diffuse reflectance spectra of (a) Zn-Al LDH and (b) Zn-Al/HMCA LDH films.

Conclusions

HMCA was intercalated into interlayer spaces of Zn-Al LDH by simple potentiometric electrolysis, and the ZnAl-LDH/HMCA film prepared on a Pt electrode showed an excellent UV-ray absorption property.

Reference

1. W. Sun et al., *Mater. Chem. Phys.*, **107**, 261–265 (2008).