Synthesis and Ultraviolet-ray-shielding Property of Organic UV-absorbent Intercalated Layered Zinc Hydroxide

Sumio Aisawa, Eri Ishida, Satoshi Takahashi, Hidetoshi Hirahara, and Eiichi Narita*
Graduate School of Frontier Materials and Functional Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551

(Received January 14, 2005; CL-050069)

The hybridization between organic ultraviolet (UV)-absorbent and layered zinc hydroxide (LZH) by the coprecipitation reaction has been investigated. Various organic UV-absorbents were intercalated into the LZH interlayer space, and the resulting UV-absorbent/LZH was found to have high transparency in the visible region and superior shielding ability in the UV region.

A preparation and characterization of the organic–inorganic hybrid materials have received considerable attentions for the development of novel structure and characterization in recent years.[1–3] The intercalation of organic molecules for the inorganic layered materials is widely used as a synthesis of the organic–inorganic hybrid materials. One of the inorganic layered compounds, LZH, is possible to intercalate various guest molecules and ions for the interlayer space.[4–6] On the other hand, UV-ray is a specific part of the sun's entire spectrum of wavelengths and known as a cause of skin cancer. Various inorganic UV-scatter and organic UV-absorbent materials have been used as sunscreen substances for purpose of the alleviation of the healthy damage by UV-ray. However, as a use to sunscreen materials for skin, the organic UV-absorbent materials have a safety problem using at high concentration. Therefore, He et al. reported the intercalation of organic UV-absorbents for the layered double hydroxide.[7] In this work, we attempted to synthesize the UV-absorbent/LZH by the coprecipitation reaction with intention of the application for novel sunscreen materials.

The coprecipitation of UV-absorbent with the LZH precipitate was mainly investigated using *p*-amino benzoic acid (PABA). $Zn(NO_3)_2$ solution was added dropwise to the UV-absorbent solution such as PABA, 2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid (HMBP), 4-hydroxy-3-methoxy benzoic acid (HMBA), 4,4′-diaminostilbene-2,2′-disulfonic acid (DASDSA), 4-hydroxy-3-methoxycinnamic acid (HMCA), and urocanic acid (UA) with stirring under a nitrogen atmosphere at 298 K. The solution pH was controlled by dropwise addition of NaOH solution. The precipitate was collected by centrifugation after aging for 1 h.[8] The solid product was washed with distilled water and dried in a vacuum oven at 313 K for 24 h.

The influence of the solution pH and Zn/PABA molar ratio for the degree of PABA coprecipitation was investigated, and the results are shown in Table 1.[9] The degree of PABA coprecipitation became the maximum (31%) at pH 7.0 and decreased with increasing the solution pH, because the formation of $Zn(OH)_2$ was taken precedence with increasing the amount of OH^- in the solution. As the acid–base equilibrium constant of PABA is $pK_a = 4.7$, PABA is probably intercalated as anion form into the LZH. The amount of PABA intercalated was agreed with

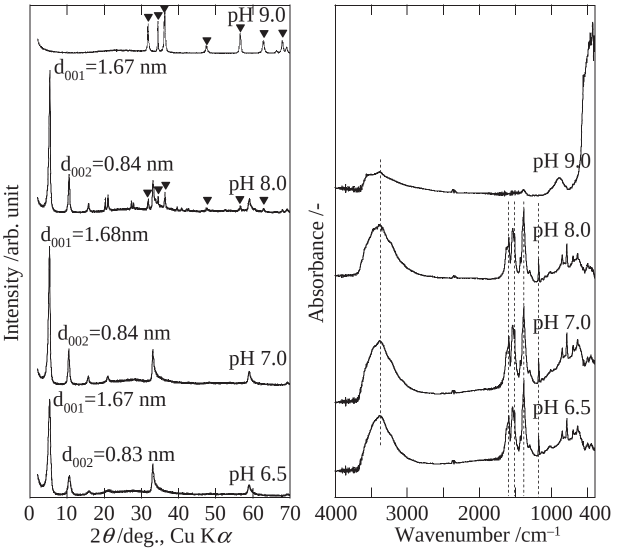

Figure 1. XRD patterns and FT-IR spectra of PABA/LZH ▼: ZnO.

Table 1. Degree of UV-absorbent coprecipitation, XRD data, and chemical compositons of solid products

UV-absorbent	pH	Zn/UV-absorbent molar ratio	Coprecipitation (%)	Chemical composition	d_{001} and d_{002}/nm
PABA	6.5	1.0	12	$[Zn(OH)_{1.79}PABA_{0.12}][(NO_3)_{0.09}\cdot 1.51H_2O]$	1.67, 0.83
PABA	7.0	1.0	31	$[Zn(OH)_{1.67}PABA_{0.30}][(NO_3)_{0.03}\cdot 1.92H_2O]$	1.68, 0.84
PABA	8.0	1.0	11	$[Zn(OH)_{1.81}PABA_{0.10}][(NO_3)_{0.09}\cdot 0.83H_2O]$	1.67, 0.84
PABA	9.0	1.0	2.0	ZnO	—
PABA	7.0	0.5	8.5	ZnO	—
PABA	7.0	2.0	40	$[Zn(OH)_{1.75}PABA_{0.22}][(NO_3)_{0.03}\cdot 0.92H_2O] + ZnO$	1.67, 0.84
HMBP	7.0	1.0	7.2	ZnO	—
HMBA	7.0	1.0	28	$[Zn(OH)_{1.69}HMBA_{0.29}][(NO_3)_{0.02}\cdot 1.48H_2O]$	2.15, 1.07
DASDSA	7.0	1.0	5.1	$Zn(OH)_2$	—
HMCA	7.0	1.0	36	$[Zn(OH)_{1.64}HMCA_{0.35}][(NO_3)_{0.01}\cdot 1.63H_2O]$	2.60, 1.30
UA	7.0	1.0	80	$[Zn(OH)_{0.92}UA_{1.05}][(NO_3)_{0.03}\cdot 2.01H_2O]$	—

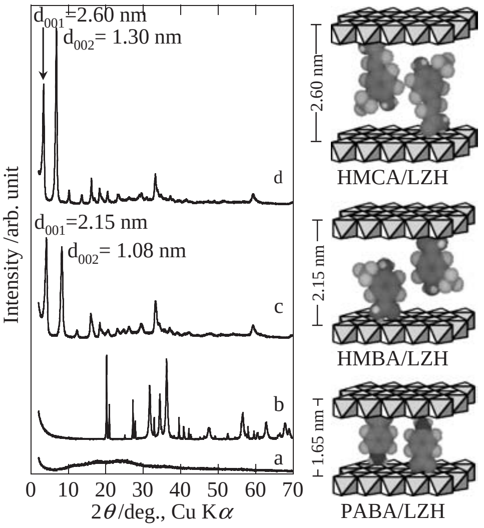

Figure 2. XRD patterns and schematic illustrations of UV-absorbent/LZH. (a) UA, (b) DSADAS, (c) HMBA, and (d) HMCA.

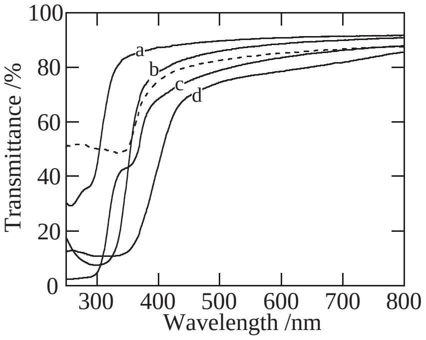

Figure 3. UV–vis spectra of UV-absorbent/LZH. (a) HMBA, (b) UA, (c) PABA, and (d) HMCA. Dotted line: $Zn(OH)_2$.

stoichiometry of LZH, and the small amount of NO_3^- was also intercalated as coexistent anion. At low Zn/PABA molar ratio = 0.5, the solid products was ZnO. In the case of Zn/PABA = 2.0, the degree of PABA coprecipitation was 40%. The solid product had the expanding layered structure and the excess of Zn^{2+} formed ZnO as a by-product. Accordingly, the synthesis of the UV-absorbent/LZH was carried out at pH 7.0 and Zn/UV-absorbent = 1/1.

The XRD patterns and FT-IR spectra of the solid products are shown in Figure 1.[10,11] In the cases of pH 6.5, 7.0, and 8.0, the solid products possessed the well ordered layered structure with the basal spacing, $d_{001} = 1.67$ and $d_{002} = 0.84$ nm. From FT-IR, a broad absorption peak in the 3000–3600 cm^{-1} region is assigned to O–H group stretch of hydroxide basal layer and interlayer or absorbed water. The adsorption peaks, N–H stretch at 1640 cm^{-1}, COO^- stretch at 1180 and 1540 cm^{-1}, of the intercalated PABA were observed. The strong adsorption peak of the cointercalated NO_3^- was also shown at 1385 cm^{-1}. In the case of pH 9.0, sharp diffraction peaks were observed without layered structure which corresponded to ZnO. In the low-frequency region, the absorption peaks of the spectra corresponded to the lattice vibration modes are attributed to Zn–O (900 cm^{-1}) and O–Zn–O (450–550 cm^{-1}) vibrations. A broad and weak absorption peak in the 3000–3600 cm^{-1} region is assigned to O–H group stretches of absorbed water. The XRD patters of the UV-absorbent/LZH and the degree of the UV-absorbent coprecipitation are shown in Figure 2 and Table 1, respectively. The UA/LZH did not show the layered structure in spite of the high degree of UA coprecipitation (80%). HMBP and DASDSA were hardly intercalated for the LZH because the sulfonate anion thought to be grafted for the LZH basal layer. The HMBA/LZH and HMCA/LZH had the expanding layered structure, $d_{001} = 2.15$ and 2.60 nm, demonstrating that UV-absorbent was intercalated for the LZH interlayer space. As the thickness of the LZH basal layer is 0.48 nm, the interlayer space is calculated as 1.19 (PABA), 1.67 (HMBA), and 2.12 nm (HMCA). These values support that organic UV-absorbents are vertically oriented with formation of direct bonding to the LZH basal layers as shown in Figure 2. From the observation of SEM photographs, the UV-absorbed/LZH had a plate-like morphology, and particle size was 0.5–1.0 µm. On purpose to estimate UV-shielding ability of the UV-absorbent/LZH, the UV–vis spectra of the UV-absorbent/LZH are shown in Figure 3.[12] The transmittance of the HMBA/LZH was 85% in the visible light region and 30–40% in the range 250–300 nm. UA/LZH had high transmittance in the 400–800 nm and good UV-shielding ability in the 250–340 nm range. The PABA/LZH showed excellent UV-shielding ability in the 250–300 nm range and well transparency (80%) in the visible right region. The HMCA/LZH had low transparency in the visible region and good UV-shielding ability, 10%, in the 250–400 nm. These results confirmed that all UV-absorbent/LZH have superior UV-shielding ability.

The UV-absorbent/LZH with good UV-shielding ability can be prepared by the coprecipitation reaction. The UV-absorbent/LZH would be received considerable attention in the future as novel sunscreen materials.

This work was supported by the program "Development of Rechargeable Lithium Battery with High Energy/Power Density for Vehicle Power Sources" of the Industrial Technology Research Grant Program from New Energy an Industrial Technology Development Organization of Japan (NEDO) and the Sasakawa Scientific Research Grant from The Japan Science Society.

References and Notes

1 "Inorganic Materials," 2nd ed., ed. by D. W. Bruce and D. O'Hare, John Wiley and Sons Ltd., Chichester (1997).

2 S. Aisawa, H. Hirahara, S. Takahashi, Y. Umetsu, and E. Narita, *Chem. Lett.*, **33**, 306 (2004).

3 S. Sasaki, S. Aisawa, H. Hirahara, A. Sasaki, and E. Narita, *Chem. Lett.*, **33**, 790 (2004).

4 S. Ogata, I. Miyazaki, Y. Tasaka, H. Tagaya, J. Kadokawa, and K. Chiba, *J. Mater. Chem.*, **8**, 2813 (1998).

5 S. Ogata, H. Tagaya, M. Karasu, and J. Kadokawa, *J. Mater. Chem.*, **10**, 321 (2000).

6 S. Takahashi, T. Iwasa, Y. Kanazawa, Y. Umetsu, and E. Narita, *Nippon Kagaku Kaishi*, **1997**, 502.

7 Q. He, S. Yin, and T. Sato, *J. Phys. Chem. Solids*, **65**, 395 (2004).

8 Degree of UV-absorbent coprecipitation was calculated from the amount of UV-absorbent concentration decreased by using a Shimadzu TOC-5000 before and after the coprecipitation reaction.

9 Chemical analysis data for the solid products were determined by a Shimadzu AA-6650 (Zn), a TOA Electronics IA-100 ion analyzer (NO_3^-), a Rigaku TAS-200 (H_2O), and a TOC (UV-absorbent).

10 XRD patterns were recorded on a Rigaku Rint 2200 using Ni-filtered Cu Kα radiation at 20 mA and 40 kV.

11 FT-IR spectra were recorded on a JASCO WS/IR 7300 by KBr disk method.

12 UV–vis spectra were recorded on a JASCO V 570 using diffusion refraction method.

Published on the web (Advance View) March 26, 2005; DOI 10.1246/cl.2005.630