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Preparation of organic-inorganic layered nanohybrids by intercalation of photofunctional compounds

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Nanohybrid materials consisting of Zn/Al layered double hydroxide (Zn/Al LDH) intercalated by an organic chromophore of indigocarmine were prepared to control an interlayer distance of the nanohybrids by contact with acidic gas. The thin film has the *d*-spacing of 1.8 nm. The *d*-spacing increased to 2.2 nm when this thin film contacted to HCl gas. When this thin film was left in the air, the *d*-spacing of 2.2 nm decreased to 1.8 nm. The acid treatment of the nanohybrid material also caused changes in the absorption spectrum of intercalated indigocarmine. The absorption peak of the nanohybrids was observed at 658 and 786 nm. By contact with HCl gas, absorption peak at 786 nm decreased together with the time, and only the peak at 657 nm was left. The interlayer spacing of this nanohybrids changed reversibly by absence or presence of acid.
Key words: layered double hydroxide, intercalation, indigocarmine, thin film

1. INTRODUCTION

Organic materials are intercalated as guests into an inorganic layered material, leading to the formation of organic-inorganic nanocomposites. These intercalation compounds were self-ordered materials and have the potential possibility as new functional materials. Layered double hydroxide (LDH) having positive charges is inorganic layered materials and known as an anion exchangeable clay which can intercalate various organic and inorganic anions. Lower valent metal cation, typically Zn(II), is partially substituted by higher valent metal cations, such as Al(III), thereby developing a net positive charge.

Recently, a reversible change of interlayer spacing of intercalation compounds has been reported. Fujita *et al.* reported that reversible structural transformation of interlayer spacing of intercalated 8-((*p*-(phenylazo)phenyl)oxy)octanoate in copper hydroxides occurred by the treatment of the solvent such as methanol and acetonitrile.[1] Takagi *et al.* pointed out that arrangement structure of sodium stearate into Mg/Al layered double hydroxide change reversibly between monolayer and bilayer by heat treatment. This change depended on temperature.[2]

Indigocarmine (IDC) is well known a representative dye, which forms intermolecular hydrogen bonds between the carbonyl and secondary amino groups. In our previous paper, we report that indigocarmine intercalation compound exhibit two kinds of interlayer spacings, which reversibly changed by the treatments with acid or base solution.[3] In this study, we prepared a thin film of the indigocarmine intercalation compound and investigate a change of characteristecs by the treatment with acidic gas.

2. EXPERIMENTAL

2.1 Preparation of nanocomposites of Zn/Al layered double hydroxide

The inorganic material of Zn/Al layered double hydroxide (Zn/Al LDH) was prepared through precipitation method starting from a homogeneous solution containing a mixture of $Zn(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and urea. The Zn:Al atomic ratio in the starting solution was adjusted to 7:3. Typically, 13.74 g of $Zn(NO_3)_2 \cdot 6H_2O$, 7.44 g of $Al(NO_3)_3 \cdot 9H_2O$ and 60.06 g of urea were mixed together in 2000 ml of water. This solution was vigorously stirred for 12 h at 363 K. After the reaction, the precipitate was filtered, and washed by using distilled water and dried for 12 h at 333 K.

2.2 Intercalation reaction of Zn/Al layered double hydroxide with indigocarmine

The Zn/Al layered double hydroxide was calcined at 773 K for 3 h to remove carbonate gas in interlayer. A 0.12 g of indigocarmine was dissolved in 80 ml of degassed water. A 0.20 g of calcined Zn/Al layered double hydroxide was then added to the solution (twofold excess of the indigocarmine), and the mixture was stirred under N_2 at 333 K for 3 h. The product was filtered, washed with distilled water, and dried under a reduced pressure at room temperature.

2.3 Acid treatment

The IDC intercalation compound suspension was obtained by ultrasonic treatment and stirred in distilled water. The thin film of the IDC intercalation compound was made on washed slide glass by drawing up slide glass from suspension. Drawing up rate was about 0.15 m/1 h. Drawing up numbers were 2, 5, and 10 times.

The thin film of the IDC intercalation compound was put in the bottle which put 50 ml of 2 M-HCl solution not to touch HCl solution. The bottle was shut tight, and left for 1 week at room temperature.

All reactions were carried out by using commercial reagents (of analytical-reagents grade) without further purification.

2.4 Physical measurement

Powder X-ray diffraction (XRD) spectra were recorded on a Rigaku powder diffractometer, using Cu Kα (filtered) radiation (λ = 0.154 nm) at 40 kV and 20 mA between 1.8 and 50 degrees in 2 θ. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of powdered samples up to 873 K were carried out at a heating rate of 10 K/min in flowing N_2 using a Seiko SSC 5000 thermal analysis system. Absorption spectra were recorded on a Shimazu UV-2200A spectrophotometer.

3. RESULTS AND DISCUSSION

Thermal characteristics of Zn/Al layered double hydroxide were determined by TG analysis. Two weight loss of Zn/Al layered double hydroxide was observed up to 500 K and between 700 and 800 K. The first region corresponded to the dehydration of absorbed water molecules and interlayer water molecules. The second region between 700 and 800 K corresponded to desorption of indigocarmine and the dehydration of OH group of the Zn/Al layered double hydroxide layers. The total weight loss was larger than that of the Zn/Al layered double hydroxide. Therefore, we concluded that indigocarmine was incorporated into the Zn/Al layered double hydroxide.

The XRD pattern of the Zn/Al layered double hydroxide showed a strong clear peak at near 0.76 nm as shown in Fig. 1(a). By calcination of the Zn/Al layered double hydroxide at 773 K, no clear peaks were observed. The *d*-spacing of the products were increased from 0.76 nm to 1.8 nm by the intercalation reaction of the calcined Zn/Al layered double hydroxide with indigocarmine as shown in Fig. 1(b), (c). From the size of indigocarmine and interlayer spacing, it was concluded that indigocarmine molecule was monolayer arrangement between the layers. The peak intensity of the product in the XRD patterns depended on the number of drawing up times.

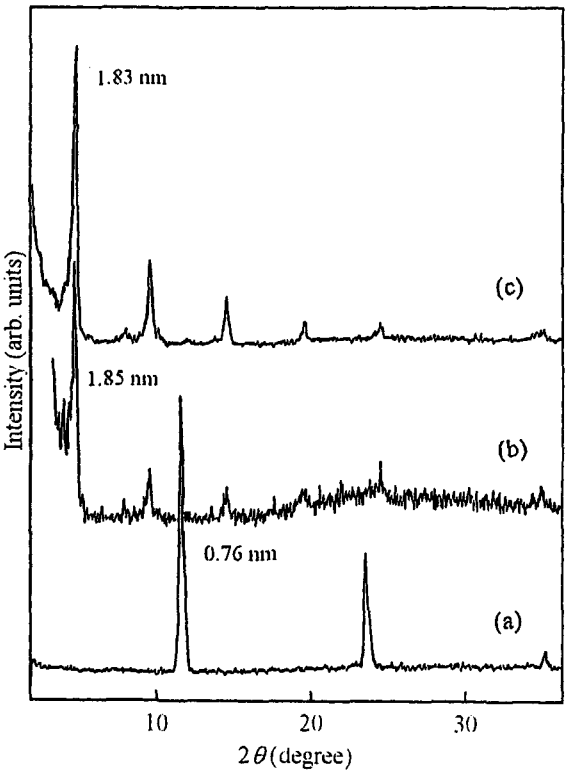

Fig. 1 XRD patterns of (a)Zn/Al layered double hydroxide, the thin films of drawing up number of (b)2 times, and (c)5 times.

After the acid treatment, the *d*-spacing of the products increased from 1.8 nm to 2.20 nm as shown in Fig. 2. It indicated that the interlayer spacing of indigocarmine intercalation compound increased by contact with acid gas. In thin film of 10 times drawing up, the peak at 1.93 nm was remained. This suggested that the effect of hydrochloric acid gas occurred from the surface of the film. Thickness of thin film of 10 times drawing up was largeer than other films, therefore it needed more time to change its structure than 5 times drawing up. This increment of interlayer spacing was considered that intercalated indigocarmine between the layers changed from monolayer arrangement to bilayer arrangement due to intermolecular interaction developed by acid gas. In our previous paper[3], we measured the IR spectra. The IR spectra of the product having *d*-spacing of 1.8 nm showed the sharp peak at 1040 cm^{-1} and the broader peak at 1196 cm^{-1}. These peaks are assigned to the characteristic of S-O vibrations in $R\text{-}SO_3$. Furthermore, the IR spectra of the product having 2.2 nm showed the sharp peaks at 1610 cm^{-1} and 1637 cm^{-1} which are assigned to the intermolecular hydrogen bonds between the carbonyl groups and secondary amino groups in indigocarmine and the doubly conjugated carbonyl band, respectively. However, in the case of product having 1.8 nm there was not observed the peak at 1637 cm^{-1}. Therefore, it meant that for the product having *d*-spacing of 1.8 nm the intermolecular hydrogen bond of indigocarmine was stable in the layered double hydroxide interlayer. However, it was considered that for the product having *d*-spacing of 2.2 nm the intermolecular hydrogen bond of indigocarmine is inhibited. From these result, it was suggested an another interaction between the protonated secondary amino groups and sulfonate anions.

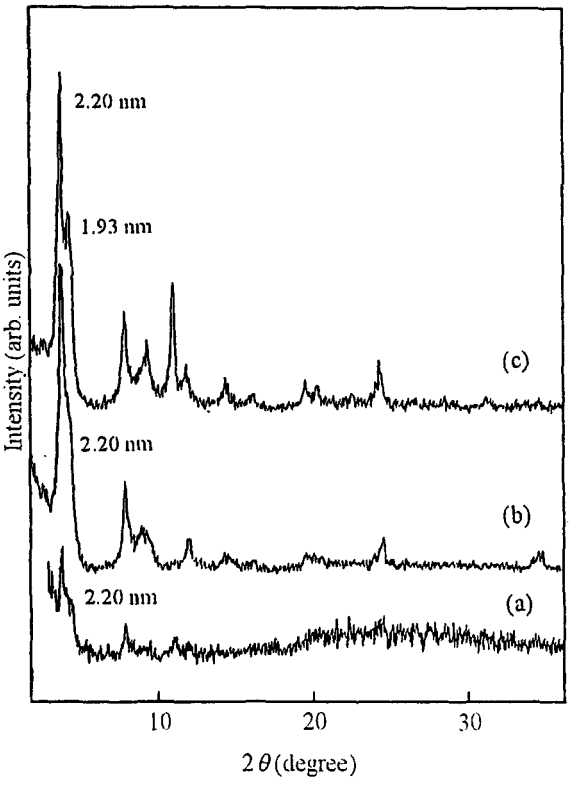

Fig. 2 XRD patterns of thin film of the reaction products after the acid gas treatment, drawing up number of (a)2 times, (b)5 times, and (c)10 times.

The absorption spectra of the product and that after the acid treatment were recorded as shown in Fig. 3. The absorption peaks of the product were observed at 658 and 786 nm. For the absorption spectrum of thin film after 5 min treatment, the peak at 786 nm decreased as shown in Fig. 3(b). Furthermore, in the absorption spectrum after 6 h, the peak at 786 nm disappeared and only the peak at 658 nm was observed as shown in Fig 3(c). It was suggested that the orientation of indigocarmine was different with that after the treatment by the acid gas.

Furthermore, we have examined whether the interlayer spacing of the product after the acid gas treatment changes reversibly or not. In the case of the

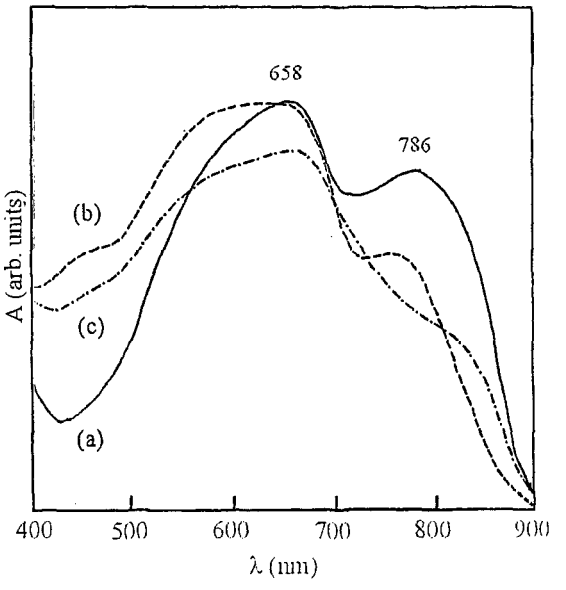

Fig. 3 Absorption spectra of (a)the reaction product, (a) treated by HCl gas (b)for 5 min, and (c)for 6 h.

thin film, the interlayer spacing of 2.20 nm decreased to 1.83 nm by standing in the air as shown in Fig. 4. In the case of the bulk state, the interlayer spacing of 2.2 nm decreased to 1.8 nm only by the treatment in base solution. But, in the case thin film, the peak at 2.2 nm decreased in a short time by allowing the film to stand in air, and returned to interlayer spacing similar to that before contact with the hydrochloric acid gas. This suggested that the interlayer spacing increased under the presence of acid.

4. CONCLUSION

We have succeeded to prepare thin film of intercalation compound of indigocarmine into the Zn/Al layered double hydroxide, which shows reversible change of interlayer spacing by contact with acid gas. The interlayer spacing of thin film increased quickly. Because the thin film has a large surface area. They have potential as indicator to the acid.

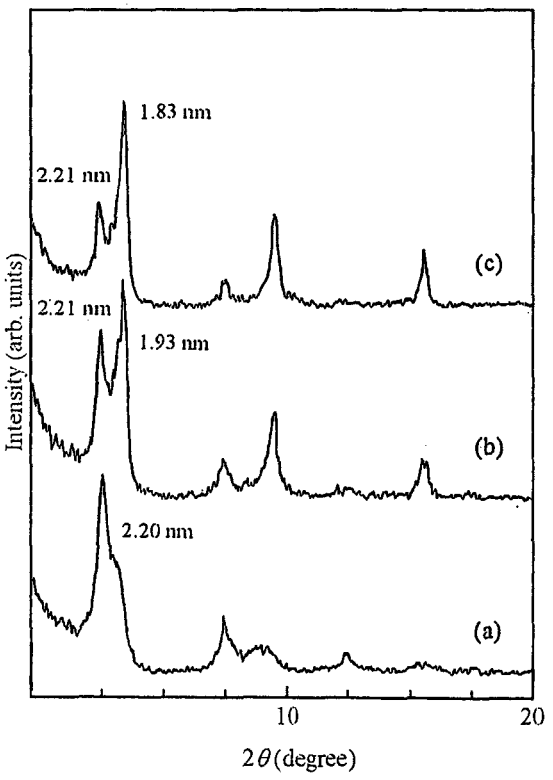

Fig. 4 XRD patterns of the reaction product (a)drawing up number of 5 times after the acid treatment for 1 week, (a) put in the air (b)for 30 min, and (c)for 2 days.

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