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Direct coating for layered double hydroxide/4,4′-diaminostilbene–2,2′-disulfonic acid nanocomposite with silica by seeded polymerization technique

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Abstract

Organic ultraviolet (UV) ray absorbents have been used as sunscreen materials, but may pose a safety problem when used at high concentration. In order to prevent direct contact of organic UV rays absorbent by the human skin, an organic UV absorbent such as 4,4′-diaminostilbene-2,2′-disulfonic acid (DASDSA) was intercalated into Zn_2Al-layered double hydroxide (Zn_2Al-LDHs) by coprecipiation reaction. The problem of deintercalation of organic molecules from LDHs by the anion exchange reaction with carbonate ion could be greatly depressed by forming a protection film of silica on the surface. Zn_2Al-LDH/DASDSA was directly coated with silica by means of a polymerization technique based on the Stöber method. The deintercalation behavior as well as UV-shielding properties were investigated for coated particles.

Keywords: Ultraviolet absorbent; Layered double hydroxide; Silica; Seeded polymerization; Coating; Deintercalation

1. Introduction

It is well known that ultraviolet (UV) ray in sun light causes several problems such as photodegradation of organic materials and damages human health, e.g., causes sunburn, suntan, acceleration of aging, cancer, etc. [1–3]. Organic materials such as 4,4′-diaminostilbene-2,2′-disulfonic acid (DASDSA), 4-hydroxy-3-methoxybenzoic acid, 2-hydroxy-4-methoxybenzophenon-5-sulfonic acid, *p*-aminobenzoic acid and urocanic acid possess excellent UV ray absorption ability [2] and have been used as sun-care products. However, it is suspected that organic UV ray absorbents may pose a safety problem when they are used at high concentrations, since they tend to be absorbed into the body through the skin. One of the solutions to this problem may be the incorporation of organic materials in nanospaces of inorganic materials to avoid direct contact of organic molecules and skin. Layered double hydroxides (LDHs) of the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[A^n_{x/n}]^{x-}\cdot mH_2O$ consist of hydrotalcite-like layers and exchangeable interlayer anions [4–8]. The unique anion exchange capability of LDHs meets the requirements of inorganic matrices for encapsulating UV absorbents with negative charge in aqueous media. However, organic UV absorbents incorporated in LDH are easily deintercalated by the anion exchange reaction with carbonate ions since the selectivity of ion exchange of carbonate is quite higher. In order to depress the deintercalation of organic UV-absorbent molecules from Zn_2Al-LDH layer, the Zn_2Al-LDH/UV-absorbing molecules could be coated with amorphous silica. A number of studies have been reported on coating of different kinds of fine particles with silica [9–17]. The shell of the latter was produced to provide the cores with different reacting sites, to alter their conductivity and optical properties, to increase the stability of the dispersion, etc. It was demonstrated that the modification of the Stöber process [18], consisting of the hydrolysis of tetraethylorthosilicate (TEOS) in the presence of dispersed particles, yielded a rather uniform

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smooth layer of silica, the thickness of which could be controlled by varying the experimental conditions [10,11].

In this work, a method for directly coating Zn_2Al-LDH/DASDSA with silica shell by a seeded polymerization technique was proposed. The effect of different silica weight percent and ammonia molar ratio on deintercalation behavior was investigated. UV-shielding properties were also investigated for coated particles.

2. Experimental

2.1. Synthesis

Distilled and deionized water was used in all preparations. The water was boiled immediately before use. Zn_2Al-LDH/DASDSA was prepared by coprecipiation reaction reported by He et al. [19] as follows. After dissolving 0.025 mol of DASDSA into 200 cm^3 of NaOH aqueous solution (0.4 mol dm^{-3}) at room temperature, 200 cm^3 of mixed nitrate solution containing 0.05 mol of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.025 mol of $Al(NO_3)_3 \cdot 9H_2O$, was added dropwise to the vigorously stirred DASDSA–NaOH mixed solution at room temperature over a period of 60 min, where the solution pH was maintained at 8–9 by the simultaneous addition of 1 mol dm^{-3} NaOH solution. The resulting slurry was crystallized at 70°C for 40 h. The product was isolated by centrifugal separation, washed with hot distilled water, and dried at 70°C for 18 h. The molar ratio of DASDSA/$Zn_2Al(OH)_2$ and interlayer distance, d_{003}, of the sample obtained were 0.35 and 1.55 nm, respectively. DASDSA is intercalated as bifunctional species and nitrate anion also co-intercalated with DASDSA in a layer structure as follows: $[Zn_2Al(OH)_6]$ $(DASDSA)_{0.35}(NO_3)_{0.3}(1.25\ H_2O)$. The amount of DASDSA (amount/mass %) is 30.0. The water content (amount/mass %) is 5.24.

LDH/DASDSA powder was coated with 5–20 weight percent of silica as follows. After dispersing LDH/DASDSA powder in TEOS/ethanol mixed solution, predetermined amounts of water and 29 wt% ammonia aqueous solutions were added stepwise. The reaction time and temperature were 45 min and 40°C, respectively. The slurry was filtered, washed and dried. The molar ratio of ammonia/TEOS was varied from 0 to 20 to investigate its effect on the efficiency of coating process.

For comparison, LDH/DASDSA powders were coated with silica using sodium silicate precursor as follows. After dissolving the predetermined weight of sodium silicate in 20 cm^3 H_2O, the solution was heated at 95°C with the subsequent addition of HCl to precipitate amorphous SiO_2. The precipitate was centrifuged, washed and dispersed again in 100 cm^3 H_2O, and then LDH/DASDSA powder was added. The presence of LDH/DASDSA during hydrolysis of sodium silicate could lead to collapse of LDH layer structure (by HCl), after stirring for 1 h, the precipitate was centrifuged and dried at 110°C for 3 h.

2.2. Characterization

The crystalline phase was determined by X-ray powder diffraction analysis (SHIMADZU, XD-01) with Cu$K\alpha$ radiation. The content of organic UV absorbent in LDH layer structure was determined by UV absorption specrophotometry (SHIMADZU, UV-2450). The UV-shielding properties of non-coated and coated samples were evaluated by measuring the transmittance spectra of thin films' uniformly dispersed sample powders with a UV-Vis spectrophotometer (SHIMADZU, UV-2450), where 2 g of the sample, 4 g of nitrocellulose of industrial grade, 10 g of ethyl acetate, 9 g of butyl acetate were mixed uniformly using the paint shaker and 100 g of zirconia ball, which is 2.7 mm in diameter, for 40 h. The dispersion mixture was applied onto a quartz glass plate with an applicator. Thickness of the film was 12.5 μm. Deintercalation test was conducted using 0.5 g of coated and non-coated LDH/DASDSA at 50°C. After dispersing the sample powder in 40 cm^3 water for 30 min with a magnetic stirrer, 10 cm^3 of 0.1 mol dm^{-3} Na_2CO_3 aqueous solution was added, and then the slurry solutions were taken at different times and filtered to determine the amount of DASDSA deintercalated in the solution by UV absorption specrophotometry. A scanning electron microscope (Hitachi S 4100) was used to study the surface morphology of the samples at various magnifications.

3. Results and discussion

The powder X-ray diffraction patterns of non-coated and different percentages of silica-coated Zn_2Al-LDH/DASDSA powders using TEOS are shown in Fig. 1. The pristine Zn_2Al-LDH had a well-developed layer structure. Although the peak intensity somewhat decreased by increasing the weight percent of silica, the peak position hardly changed.

It is known that DASDSA is soluble in alkaline media. So, the presence of ammonia (catalyst for hydrolysis of TEOS) in the coating process may cause deintercalation of DASDSA molecules from the layer structure by the anion exchange reaction with OH^-. When the molar ratio of NH_3/TEOS was kept constant at 20, the amount of ammonia added to precipitate silica increased with increasing silica weight percent. Accordingly, the percent of deintercalated DASDSA molecules from layer structure increased as shown in Fig. 2.

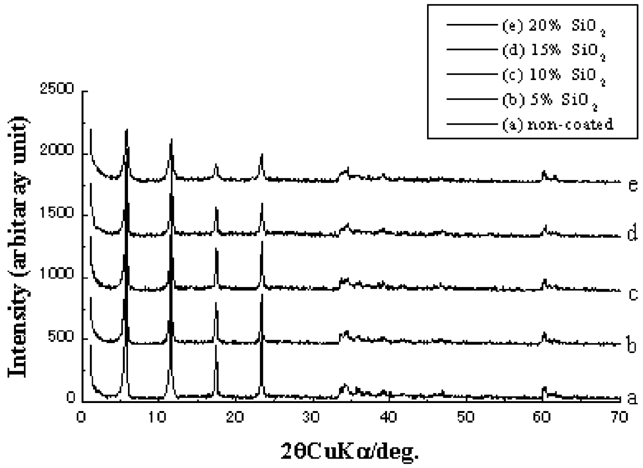

Fig. 1. Powder X-ray diffraction patterns of Zn_2Al-LDH/DASDSA (a) non-coated; coated with (b) 5, (c) 10, (d) 15 and (e) 20 wt% SiO_2 using TEOS with NH_3/TEOS molar ratio of 20.

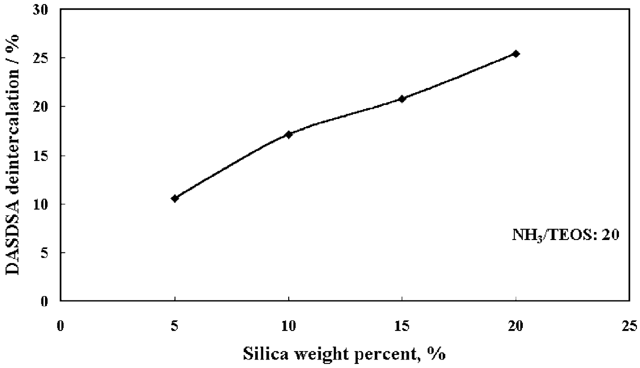

Fig. 2. Degree of deintercalation of DASDSA from Zn_2Al-LDH/DASDSA during the coating of various amounts of SiO_2 using TEOS with NH_3/TEOS molar ratio of 20.

Table 1
DASDSA content in LDH layer structure after coating with silica by seeded polymerization and dip-coating methods

Silica weight percent (%)	DASDSA content (amount/mass %)	
	Seeded polymerization	Dip coating
0	30	30
5	26.82	—
5.5	—	29.7
10	24.86	—
15	23.75	—
20	22.37	—
21	—	29.64

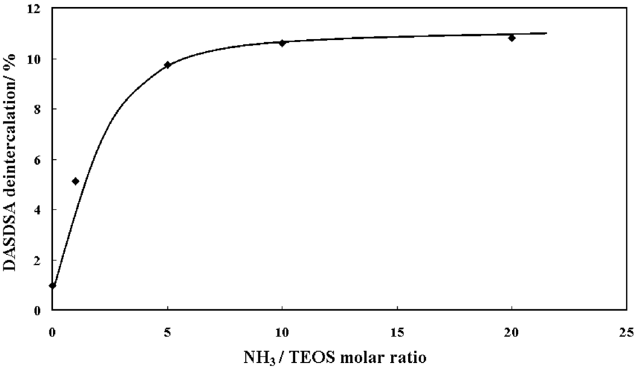

Fig. 3. Effect of NH_3/TEOS molar ratio on the deintercalation of DASDSA from Zn_2Al-LDH/DASDSA during the coating of 5 wt% SiO_2.

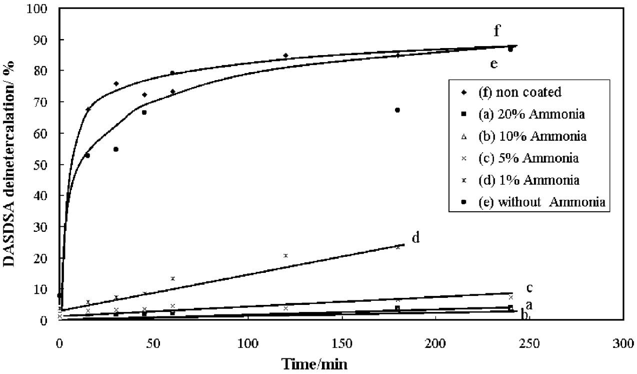

Fig. 4. Deintercalation profiles of DASDSA from Zn_2Al-LDH/DASDSA/silica in 0.02 mol dm^{-3} Na_2CO_3 aqueous solution at 50°C, where Zn_2Al-LDH/DASDSA was coated with silica using TEOS of quantity which precipitates 5 wt% SiO_2 on Zn_2Al-LDH/DASDSA and NH_3/TEOS molar ratio of (a) 20, (b) 10, (c) 5, (d) 1 and (e) 0. (f) Non-coated Zn_2Al-LDH/DASDSA.

The LDH/DASDSA formula after coating with silica is $[Zn_2Al(OH)_6]$ $(DASDSA)_{0.35}(NO_3)_{0.3}(1.25\ H_2O)/SiO_2 \cdot nH_2O$. During seeded polymerization coating DASDSA is deintercalated due to the presence of ammonia. Accordingly, after the coating step, the DASDSA content in LDH layer structure is decreased with increasing silica weight percent. On the other hand, DASDSA content is slightly decreased after coating by the dip-coating method as shown in Table 1.

In order to depress the deintercalation of DASDSA during the coating process, the molar ratio of NH_3/TEOS was decreased. The degree of deintercalation of DASDSA during the coating step of 5 wt% of silica as a function of NH_3/TEOS molar ratio is shown in Fig. 3. The degree of deintercalation of DASDSA increased from 1% to 9.5% with increasing NH_3/TEOS molar ratio from 0 to 5 and then was almost constant. It was clear that decreasing NH_3/TEOS molar ratio helps to decrease the deintercalation of DASDSA molecules through the coating process, but it suppressed the precipitation of SiO_2 on the Zn_2Al-LDH/DASDSA surface.

The degree of deintercalation of DASDSA from Zn_2Al-LDH/DASDSA/silica in 0.02 mol dm^{-3} Na_2CO_3 aqueous solution at 50°C is shown in Fig. 4, where Zn_2Al-LDH/DASDSA was coated with silica using a quantity of TEOS which precipitates 5 wt% SiO_2 on

Zn_2Al-LDH/DASDSA and various amounts of ammonia. It is seen that ca. 85% of DASDSA was deintercalated from Zn_2Al-LDH/DASDSA without silica coating by the ion exchange reaction with CO_3^{2-} for 240 min (Fig. 4f). When ammonia was not used (Fig. 4e), no noticeable amount of silica precipitated and, consequently, the deintercalation profile was almost identical with Zn_2Al-LDH/DASDSA without silica coating. Therefore, it is essential to use ammonia as a catalyst for the hydrolysis of TEOS to precipitate SiO_2 on the surface of LDH/DASDSA. It is clear that increasing NH_3/TEOS molar ratio leads to the decrease of deintercalation of DASDSA molecules from the layer structure. The degree of deintercalation of DASDSA could be decreased to less than 10% using 10 or more of NH_3/TEOS molar ratio.

The degree of deintercalation of DASDSA from Zn_2Al-LDH/DASDSA coated with different amounts of silica in 0.02 mol dm^{-3} Na_2CO_3 aqueous solution at 50°C is shown in Fig. 5, where Zn_2Al-LDH/DASDSA was coated with silica using TEOS (NH_3/TEOS molar ratio of 20) and Na_2SiO_3. As expected, from Fig. 5 it was clear that coating with silica greatly suppressed the deintercalation of the DASDSA from the layer structure. The deintercalation percentage decreases from 85% to less than 10%. Also, it is clear that increasing the silica coating percent from 5 to 20 wt% did not have a significant decrement in the deintercalation percent. It can be seen, however, that the deintercalation degree for silica-coated LDH/DASDSA using TEOS precursor is lower than the one using sodium silicate precursor, indicating that the coating process of TEOS precursor is more efficient than that of the sodium silicate one.

The UV ray can be divided into three parts by wavelength as UV-A (320–400 nm), UV-B (280–320 nm) and UV-C (200–280 nm). Since UV-C and most of UV-B are absorbed by the ozone layer in the upper atmosphere, the UV ray in the sunlight which reaches the ground is mainly UV-A (90–99%), and UV-B is also contained slightly (1–10%). Therefore, the UV-shielding materials are expected to absorb UV rays less than 400 nm wavelength. In order to evaluate the UV-shielding ability of silica-coated and non-coated Zn_2Al-LDH/DASDSA, the UV-Vis transmittance spectra of the samples were determined, and results are shown in Fig. 6. Non-coated powder showed excellent UV-shielding ability and transparency in the visible light region. The UV-shielding ability tended to decrease with increasing silica weight percent, but 5 wt% silica-coated sample retained almost identical UV-shielding ability and transparency in the visible light region.

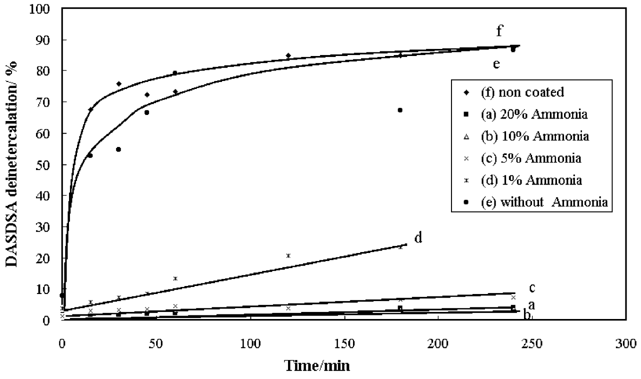

Fig. 5. Deintercalation profiles of DASDSA from Zn_2Al-LDH/DASDSA, non-coated and coated, with different amounts of silica in 0.02 mol dm^{-3} Na_2CO_3 aqueous solution at 50°C. (a) Non-coated Zn_2Al-LDH/DASDSA; (b), (c), (d) and (e) were coated with 5, 10, 15 and 20 wt% SiO_2 using TEOS (NH_3/TEOS molar ratio of 20), whereas (f) and (g) were coated with 5.5 and 21.3 wt% SiO_2 using Na_2SiO_3.

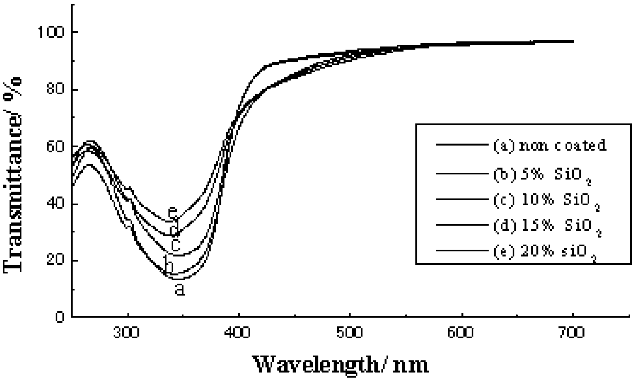

Fig. 6. UV-Vis tranmittance spectra of thin films of Zn_2Al-LDH/DASDSA of (a) non-coated; coated with (b) 5, (c) 10, (d) 15 and (e) 20 wt% SiO_2 using TEOS (NH_3/TEOS molar ratio of 20).

Figs. 7a and b show the morphology of non-coated and 5 wt% silica-coated Zn_2Al-LDH/DASDSA obtained by a scanning electron microscope at different magnifications. The micrographs show agglomerates of compact and non-porous plate-like structures which are typical of LDH particles. The surface of the silica-coated sample looks smoother than that of the non-coated one. It may be evidence of the precipitation of silica on the surface of Zn_2Al-LDH nanocomposites.

4. Conclusion

Silica coating helps in decreasing the deintercalation of organic from the layer structure. Deintercalation of DASDSA molecules from silica-coated LDH using TEOS precursor is lower than that using sodium silicate precursor which may suggest that the coating process using TEOS is more efficient than that using the sodium silicate one. The DASDSA is deintercalated through the coating process due to the presence of NH_3 in the coating process. Controlling ammonia stoichiometry to TEOS helps in decrement of the deintercalation of DASDSA molecules through the coating process. The UV-shielding ability is decreased with increasing silica

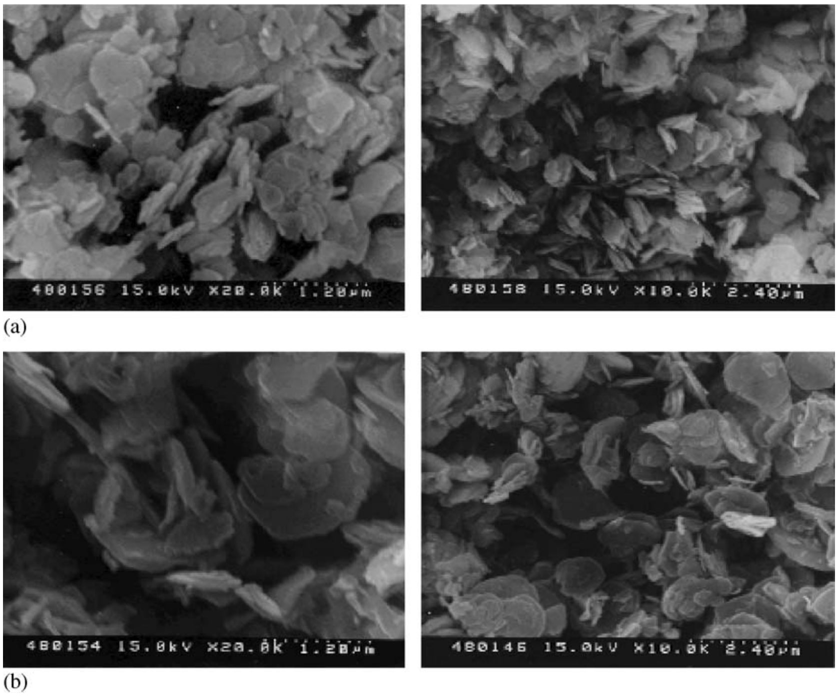

Fig. 7. Scanning electron micrographs of (a) non-coated Zn_2Al-LDH/DASDSA; and (b) 5 wt% SiO_2-coated Zn_2Al-LDH/DASDSA using TEOS (NH_3/TEOS molar ratio of 10).

weight percents, but 5 wt% silica-coated sample retained almost identical UV-shielding ability and transparency in the visible light region.

Acknowledgments

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References

[1] S. Asano, Hyoumenkagaku 15 (1994) 173.
[2] L. Diffey, Phys. Med. Biol. 36 (1991) 299.
[3] R. Neades, L. Cox, J.C. Pelling, Mol. Carcinogen. 23 (1998) 159.
[4] R. Allmann, Chimia 24 (1970) 99.
[5] R.M. Taylor, Clay Miner. 19 (1984) 591.
[6] T. Sato, S. Onai, T. Yoshioka, A. Okuwaki, J. Chem. Technol. Biotechnol. 57 (1993) 137.
[7] F. Cavani, F. Trifiro, A. Vaccari, Catal. Today 11 (1991) 173.
[8] M. Lakraimi, A. Legrouri, A. Barroug, A.D. Roy, J.P. Besse, J. Mater. Chem. 10 (2000) 1007.
[9] R.K. IIer, US patent No. 2,885,336,1959.
[10] M. Ohmori, E. Matijevic, J. Colloid Interface Sci. 150 (1992) 594.
[11] M. Ohmori, E. Matijevic, J. Colloid Interface Sci. 160 (1993) 288.
[12] A.P. Philipse, M.P.B. Van Bruggen, C. Pathmamanoharan, Langmuir 10 (1994) 92.
[13] L.M. Liz-Marzán, A.P. Philipse, J. Colloid Interface Sci. 176 (1995) 459.
[14] L.M. Liz-Marzán, M. Giersig, P. Mulvaney, Langmuir 12 (1996) 4329.
[15] T. Ung, L.M. Liz-Marzán, P. Mulvaney, Langmuir 14 (1998) 370.
[16] J.H. Adair, T. Li, K. Havey, J. Moon, A. Mecholsky, A. Morrone, D.R. Talham, M.H. Ludwig, L. Wang, Mater. Sci. Eng. R 23 (1998) 139.
[17] Q. Liu, Z. Xu, J.A. Finch, R. Egerton, Chem. Mater. 10 (1998) 3936.
[18] W. Stöber, A. Fink, E. Bohn, J. Colloid Interface Sci. 26 (1968) 62.
[19] Q. He, S. Yin, T. Sato, J. Phys. Chem. Solids 65 (2004) 395–402.