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Preparation of Layered Zinc Hydroxide/Surfactant Nanocomposite by Pulsed-Laser Ablation in a Liquid Medium

Changhao Liang, Yoshiki Shimizu,
Mitsutoshi Masuda, Takeshi Sasaki, and
Naoto Koshizaki*

*Nanoarchitectonics Research Center (NARC),
National Institute of Advanced Industrial Science and
Technology (AIST), Central 5, 1-1-1 Higashi,
Tsukuba, Ibaraki 305-8565 Japan*

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Preparation of organic/inorganic hybrid nanocomposites has attracted significant attention in the past decades. Several works have focused on the family of layered metal hydroxide materials, such as layered double hydroxides (LDHs), hydroxide double salts (HDSs), and single-metal hydroxides, because of their pronounced anion-exchange capacity[1] and important technological applications.[2] The positively charged hydroxide layer typically presents a brucite (single layer) or botallackite (triple-decker type) structure. The divalent metal hydroxides (HDSs or single-metal hydroxides) related to divalent metals such as Ni, Co, Cu, and Zn have been extensively studied.[1c,3] Especially, layered zinc hydroxide salts (referred to as LHS−Zn), intercalated with a series of organic anions, have been synthesized by coprecipitation[4] or organo derivatization reaction methods.[5] However, those LHS−Zn composites are generally poorly crystallized and exhibit turbostratic disorder. Improved characterization of the crystal structure and morphology is thus limited. We describe here for the first time the in situ formation of a layered zinc hydroxide/dodecyl sulfate (designated as ZnDS) nanocomposite in a special solution enviroment created by pulsed-laser ablation (PLA) of a zinc plate in an aqueous solution of sodium dodecyl sulfate (SDS). The resultant ZnDS composite platelet unexpectedly presents highly ordered layered structures with well-defined octagonal shapes and in a single-crystalline state. This unique structure and morphology are investigated and compared with those of LHS−Zn composites obtained by other means.

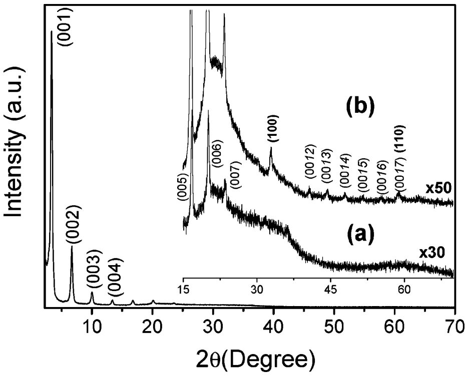

Figure 1. XRD spectra of layered ZnDS produced by PLA of Zn in an aqueous solution of SDS. Upper right inset presents the high-angle range spectra (a) from 0.001 and 0.01 M SDS solutions and (b) from 0.1 M SDS solution.

The technique of PLA in a liquid has been proven to be an effective strategy for preparing noble metal nanoparticles.[6] However, there have been few attempts to synthesize nanostructures using active metal as the target in a liquid medium. The ejected species of active metal differ essentially from that of noble metal due to their high reactivity with solutions. The final synthesized products strongly depend on the constituents of the solution involved. A layered ZnDS nanocomposite was produced in an SDS solution, while ZnO nanoparticles were formed in deionized water. In a typical experiment, a Zn plate was fixed on the bottom of a glass vessel filled with aqueous solution of 0.01 M SDS and ablated using the third harmonic (355 nm) of a Nd:YAG laser. In contrast, the PLA experiments were conducted in deionized water with more dilute (0.001 M) or concentrated (0.1 M) SDS solution (more details are described in the Supporting Information).

Figure 1 depicts X-ray diffraction (XRD) patterns of products from SDS solutions. It clearly demonstrates the formation of a layered structure. A series of (00*l*) equally spaced sharp lines were observed in the low-angle range (3°−25°) in products from different SDS solutions with the same basal spacing of 26.52 Å. There were no excess broad or asymmetric reflections in the range of high angles from products in 0.001 and 0.01 M SDS solutions (inset (a) of Figure 1). However, more high-order reflections were observed in the 0.1 M SDS solution, apart from the similar reflections in the low-angle range, despite very weak intensity, as indexed in inset (b) of Figure 1. Furthermore, two peaks with a sharp rise in intensity followed by pronounced asymmetry were revealed with plane distances of $d = 2.708$ and 1.566 Å, which is typically observed for turbostratic

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* Corresponding author. Tel: +81-29-861-4879. Fax: +81-29-861-6355. E-mail: koshizaki.naoto@aist.go.jp.

[1] (a) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1990**, *29*, 5201. (b) Clearfield, A.; Kieke, M.; Kwan, J.; Colon, J. L.; Wang, R. C. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1991**, *11*, 361. (c) Meyn, M.; Beneke, K.; Lagaly, G. *Inorg. Chem.* **1993**, *32*, 1209. (d) Fujita, W.; Awaga, K.; Yokoyama, T. *Appl. Clay. Sci.* **1999**, *15*, 281. (e) Khan, A. I.; O'Hare D. *J. Mater. Chem.* **2002**, *12*, 3191.

[2] (a) Reichle, W. T.; Kang, S. Y.; Everhardt, D. S. *J. Catal.* **1989**, *101*, 352. (b) Tagaya, H.; Sato, S.; Morioka, H.; Kadokawa, J.; Karasu, M.; Chiba, K. *Chem. Mater.* **1993**, *5*, 1431. (c) Fujita, W.; Awaga, K. *J. Am. Chem. Soc.* **1997**, *119*, 4563. (d) Choy, J. H.; Kwon, S. J.; Park, G. S. *Science* **1998**, *280*, 1589. (e) Newman, S. P.; Jones, W. *New. J. Chem.* **1998**, 105.

[3] (a) Poul L.; Jouini, N.; Fiévet, F. *Chem. Mater.* **2000**, *12*, 3123. (b) Choy, J. H.; Kwon, Y. M.; Han, K. S.; Song, S. W.; Chang, S. H. *Mater. Lett.* **1998**, *34*, 356. (c) Rojas, R.; Barriga, C.; Ulibarri, M. U.; Malet, P.; Rives, V. *J. Mater. Chem.* **2002**, *12*, 1071. (d) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.

[4] Takahashi, S.; Iwasa, T.; Kanazawa, Y.; Umetsu, Y.; Narita, E. *Nippon Kagaku Kaishi* **1997**, 502.

[5] (a) Ogata, S.; Miyazaki, I.; Tasaka, Y.; Tagaya, H.; Kadokawa, J.; Chiba, K. *J. Mater. Chem.* **1998**, *8*, 2813. (b) Ogata, S.; Tagaya, H.; Karasu, M.; Kadokawa, J. *J. Mater. Chem.* **2000**, *10*, 321. (c) Ogata, S.; Tasaka, Y.; Tagaya, H.; Kadokawa, J.; Chiba, K. *Chem. Lett.* **1998**, 237.

[6] (a) Fojtik, A.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 252. (b) Sibbald, M. S.; Chumanov, G.; Cotton, T. M. *J. Phys. Chem.* **1996**, *100*, 4672. (c) Yeh, M. S.; Yang, Y. S.; Lee, Y. P.; Lee, H. F.; Yeh, Y. H.; Yeh, C. S. *J. Phys. Chem. B* **1999**, *103*, 6851. (d) Mafuné, F.; Kohno, J.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem. B* **2001**, *105*, 5114. (e) Georgiou, S.; Koubenakis, A. *Chem. Rev.* **2003**, *103*, 349.

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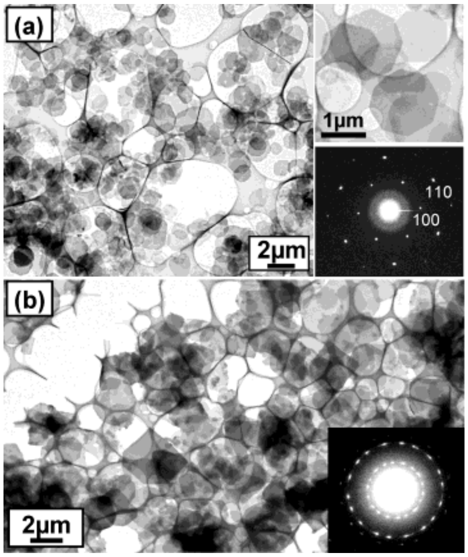

Figure 2. Representative TEM images of lamellar ZnDS platelets (a) from 0.001 or 0.01 M SDS solutions and (b) from 0.1 M SDS solution. Attached images in (a) are an enlarged morphology of a single platelet with an octagonal shape and the electron diffraction pattern from a single platelet. Inset in (b) presents the ED pattern from a gradually crumpled platelet during recording.

faults with the layers disoriented in relation to each other.[7] Although the second peak could also be indexed as (00*17*), the sharp intensity increase (compared with its neighbors) implies that at least a large part of this peak must be ascribed to the turbostratic disorder, which is indexed with combined consideration of the TEM results (vide post). Therefore, the XRD reflections are indicative of ZnDS products with long-range order, with no turbostratic faults revealed in products from 0.001 or 0.01 M SDS solutions and some stacking disorder indicated in products from 0.1 M SDS solutions. In contrast, products by PLA of Zn in deionized water revealed typical reflections (Figure S1(a)) of wurtzite ZnO, which was also confirmed by TEM observation (Figure S1(b)).

TEM images (Figure 2a) of products in 0.001 or 0.01 M SDS solutions revealed numerous lamellar thin platelets preferentially lying on the grid with irregular octagonal shapes (see the attached enlarged image) and an average diameter of 1.5 μm. The average thickness of these thin platelets was estimated to be 31.5 nm by Scherrer's formula from XRD peaks (vide supra) along the *c*-axis. Electron diffraction (ED) patterns recorded from platelets without any tilt indicated that the octagonal platelets were monocrystals lying naturally on the (00*l*) plane with clear hexagonal crystal symmetry. A few platelets with four or six edges were observed in addition to the mostly octagonal-shaped platelets in ZnDS platelets from a 0.1 M SDS solution. ED focused on one nonoctagonal platelet revealed several sets of hexagonal nets (inset of Figure 2b), which differ from the ED pattern of a single octagonal platelet. In addition, the lamellar platelets from the 0.1 M SDS solution were more quickly crumpled under electron beam irradiation than those from a lower concentration SDS solution, indicating the lower stability of ZnDS products from a 0.1 M SDS solution. The hexagonal diffraction spots (in Figure 2a) with a periodicity corresponding to a *d*-spacing of 2.71 Å could be indexed with reference to a CdI_2-type $Zn(OH)_2$ structure. The above-mentioned asymmetrical peaks in the XRD spectrum with plane spacings of 2.708 and 1.566 Å are thus indexed as (100) and (110) planes in a hexagonal structure. Zinc hydroxides have several forms at normal pressure. The most stable is α-$Zn(OH)_2$ with an orthorhombic structure.[8] However, the existence of a metastable β-$Zn(OH)_2$ with a CdI_2-type structure ($a = 3.194$ Å, $c = 4.714$ Å, space group: $D_{3d}{}^3 = \bar{C}3m$) has been confirmed at high pressure.[9] The lattice constant of a_0 was calculated to be 3.135 Å from the spacing of the adjacent (100) planes, which is slightly smaller than the reported value, implying some structure modifications. However, the lattice constant of c_0 is not determined and is included in the total basal spacing of the layered composite.

We must consider the laser-induced reaction and ionic-surfactant involvement in the assembly process in the formation of zinc hydroxide and the final layered composite. Previous studies on laser ablation at liquid–solid interfaces[10] indicated that the initial interaction between the laser light and the target surface generates plasma with high temperature, pressure, and density. The ejected active Zn species would experience strong aqueous oxidation or some other reaction since the plasma was confined in an aqueous solution. Our results indicate that aqueous oxidization in deionized water may initially lead to the formation of zinc hydroxide and hydrogen radicals $H^\bullet$ and subsequent dehydration to the formation of zinc oxide nanoparticles, similar to the processes in solvothermal oxidation of zinc metal.[11] In contrast, the charged DS ions in an SDS solution directly bonded with zinc-coordinated sites in addition to the preceding aqueous oxidation. This cooperative assembly process prevented further dehydration of zinc hydroxides from the formation of ZnO nanoparticles. A pH measurement also indicated how the different reactions proceeded. After ablation in SDS solution, the pH increased from the initial 7.0 ± 0.2 to 9.5–10.1 in the basic state, while the pH decreased from 7.0 to 5.3 in the acidic state in water.

The layered ZnDS composite was further investigated by the following experiments. A Fourier transform infrared (FT-IR) spectrum (Figure S2) revealed the presence of DS ions, hydroxyl, and intercalated water species. X-ray photoelectron spectroscopy (XPS) analysis (Figure S3) indicated prominent photoelectron peaks of Zn, O, S, and C, without traces of Na. Elemental analysis of one octagonal ZnDS platelet by energy-dispersive X-ray fluorescence spectrometer (EDX) attached to a TEM (Figure S4) yielded a similar atomic ratio of Zn:S = 1:0.34. However, the ratio of Zn:S changed to 1:0.15 if we focused on a nonoctagonal platelet, indicating that the content of intercalated DS ions was less than that of octagonal platelets. Further

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(7) Genin, P.; Delahaye-Vidal, A.; Portemer, F.; Tekaia-Elhsissen, K.; Figlarz, M. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 505.

(8) Corey, R. B.; Wyckoff. R. W. G. *Z. Kristallogr.* **1933**, *84*, 173.

(9) Baneyeva, M. I.; Popova, S. V. *Geochem. Int.* **1969**, *6*, 807.

(10) (a) Sakka, T.; Iwanaga, S.; Ogata, Y. H.; Matsunawa, A.; Takemoto, T. *J. Chem. Phys.* **2000**, *112*, 8645. (b) Zhu, S.; Lu Y. F.; Hong, M. H. *Appl. Phys. Lett.* **2001**, *79*, 1396.

(11) Li, Y. D.; Duan, X. F.; Qian, Y. T.; Yang, L.; Ji, M. R.; Li, C. W. *J. Am. Chem. Soc.* **1997**, *119*, 7869.

TG-DTA analysis (Figure S5a) revealed remarkable weight loss and endothermic peaks due to the adsorbed water, intercalated water, and coordinated hydroxyl group. The low-temperature stability and dehydration were further reflected in the XRD spectra of the ZnDS composite upon heating (Figure S5b). The layered structure was destroyed and the zinc oxide phase appeared at a low temperature. The molecular ratio of $OH:H_2O$ was calculated to be 1:0.13 from the weight loss. There were no observable differences in thermal analysis of ZnDS composites from different solutions. The overall stoichiometric formula of those octagonal ZnDS platelets based on the data and the electronic neutrality of the final composite is proposed as $Zn(OH)_{1.66}(C_{12}H_{25}SO_4)_{0.34}\cdot 0.22H_2O$, while a few nonoctagonal platelets from 0.1 M SDS should have fewer intercalated DS ions.

The essential prerequisite for assembling hybrid materials of organic anion and layered hydroxide is the formation of a positively charged inorganic layer. Two types of modified structures typically lead to anion-exchange behavior for layered divalent metal hydroxide composites (HDS, single-metal hydroxide).[1c] The low content of DS anions in the assembly in our case suggested that the ZnDS composite had a botallackite-type layer structure with a typical example of mineral hydrozincite in the formula of $[(Zn^{octa})_3(Zn^{tetra})_2(OH)_8]\cdot 2(A^-)\cdot nH_2O$.[12] One-quarter of the octahedral sites in the brucite layer are vacant in this structure, which is situated between another two tetrahedral Zn layer sheets stabilized just below and above the vacant octahedral sites. The structure and the basal spacing of the present ZnDS are very similar to those of alkyl sulfate HDSs with different divalent cations. Takahashi et al.[4] intensively studied coprecipitation of sebacic acid (SE) with zinc hydroxide as an organic anion-intercalated LHS−Zn composite. Botallackite-type $Zn_5(OH)_8(SE)\cdot mH_2O$ formed when the Zn/SE ratio was 1/0.23, while the zinc hydroxide layer was an orthorhombic structure with the SE ion directly coordinated to Zn^{2+} in the base framework when Zn/SE ratio was in a range of 1/0.31 to 1/1.3. Ogata et al.[5] investigated the organic derivative reaction of $Zn(OH)_2$ with carboxylic acids and found that the composite was also in a botallackite structure at a RCOOH/OH ratio of 0.25, but yielded a CdI_2-type layered compound of $Zn(OH)_x(RCOO)_y$ at a ratio of 0.5. Poul et al.[3a] reported the formation of a botallackite-type layered hydroxide Zn acetate by a chimie douce method but in thin crumpled sheets without any definite shape. Thus, a botallackite-type composite structure depends remarkably on the concentration of organics as well as the preparation techniques, and precise control of the preparation conditions is required. However, there was no essential difference in ZnDS products in our case due to the SDS concentration difference. Two weak asymmetric reflections were revealed only in the 0.1 M SDS solution. A comparison of the characteristics of the XRD pattern and platelet morphologies revealed no stacking faults in the octagonal platelets. The parallel and equidistant zinc hydroxide sheets are stacked along the *c* axis with the same orientation to each other; disordered stacking resulted in nonoctagonal platelets with typical asymmetric reflections by XRD. A possible structure of octagonal ZnDS platelets was proposed after considering the basal spacing, structure of zinc hydroxide, and SDS molecular size; the alkyl chains in that structure would be arranged in tilted bilayers between the hydroxide layers (Figure S6 and corresponding Supporting Information). The octagonal morphology of the platelets was presumably induced by unidirectional shifting of the hexagonal inorganic layers resulting from the self-assembled tilt arrangement of the surfactant molecules.

A layered zinc hydroxide/surfactant composite was synthesized by PLA of a metal Zn plate in an aqueous solution of the surfactant. The products were octagonal platelets with a single crystalline form in hexagonal symmetry. The detailed structure was analyzed and compared with that of the reported LHS−Zn. In the composite formation processes, the charged inorganic zinc hydroxide species were produced step-by-step by the strong reaction between the ablated Zn species and the water molecules, which concurrently experience assembling with surfactant molecules controlled by the charge-matching mechanism. The preferred coordination of hydrophilic headgroups with zinc coordination sites prevents further reaction from forming ZnO nanoparticles. Our unique and simple process, which is directly triggered by metal species without any chemical modifications, enables the generation of new types of hybrid composites by using other applicable metal targets and surfactants.

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Supporting Information Available: Experimental details, XRD pattern, and TEM images of zinc oxide, FT-IR, XPS, EDX, TG-DTA analyses, and proposed composite structure (Figures S1−S6) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] (a) Allmann, R. Z. *Z. Kristallogr.* **1968**, *126*, 417. (b) Stählin, W.; Oswald, H. R. *Acta Crystallogr.* **1970**, *B26*, 860.