Formation Process of Platelet Nanocomposites with Zinc Hydroxide and Sodium Dodecyl Sulfate Prepared by Laser Ablation in Solution

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Layered zinc hydroxide nanocomposites (Zn-NC) were prepared by laser ablation of Zn in an aqueous solution of sodium dodecyl sulfate (SDS) with various ablation times and laser fluences. At the fluence of 6.7 J/cm^2, the rectangular Zn-NC was obtained by 10 min ablation. Rectangular structures were found with different stages of Zn filling at the fluence of 2.0 J/cm^2. These results suggest that an SDS monohydrate with rectangular shape acts as the template for Zn-NC formation.

Layered hydroxides draw attention because of their interesting properties and applications of catalysts and adsorbents.[1] A layered hydroxide is composed of positively charged metal hydroxide sheets compensated by anions in the interlayers.[2] For instance, positively charged zinc hydroxide and anionic surfactant molecules of sodium dodecyl sulfate (SDS; $C_{12}H_{25}SO_4Na$) were alternately stacked to form layered zinc hydroxide nanocomposites (Zn-NC) by the charge matching effect.[3] Zn-NC with two-dimensional platelet morphology can be synthesized by laser ablation of a Zn metal target in an aqueous surfactant solution of SDS.[3,4] However, the detailed formation process of the Zn-NC has not yet been clearly revealed. In our previous study, the structure and morphology of Zn-NC depended strongly on the alkyl chain length of surfactant molecules.[5] In this letter, we prepared Zn-NC with a different structure by changing the ablation conditions of time and laser fluence. We also investigated the formation process of Zn-NC.

In this study, laser ablation in an aqueous surfactant solution of SDS with the concentration of 1.0×10^{-2} mol/dm^3 was used to prepare Zn-NC with better crystallinity.[3] A pulsed Nd:YAG laser (Continuum Powerlite Precision 8000) operating at 10 Hz with a wavelength of 355 nm and pulse width of 7 ns irradiated the Zn metal target, which was fixed on the bottom of a glass vessel filled with the solution at room temperature. The ablation time was changed from 1 to 60 min, and the laser fluence was set to 2.0 and 6.7 J/cm^2. The temperature of the solution increased by laser irradiation and reached to around 38 °C after the ablation at 6.7 J/cm^2 for 60 min. Obtained colloidal suspensions exhibited a cloudy white color. The suspensions at room temperature were dropped on copper mesh covered with an amorphous carbon film for morphological observation by a field emission scanning electron microscope (FE-SEM; Hitachi-4800). The obtained suspensions were repeatedly centrifuged and washed with deionized water several times to remove surfactant molecules in the precipitates. X-ray diffraction measurements (XRD; Rigaku RAD-C, Cu Kα irradiation) were performed for the precipitates that dried on quartz glass substrates.

Figure 1 shows XRD patterns of products prepared at 6.7 J/cm^2 for various ablation times. Sharp diffraction peaks of (00*l*) appeared with the same basal spacing of 26.6 Å for ablation exceeding 10 min, which indicates the formation of Zn-NC with regular stacking of the layers along the *c* axis.[3,6] The diffraction peaks of the product in the early stages of 1 and 10 min shifted to a lower angle compared to those obtained by ablation exceeding 10 min. This indicates that interlayer spacing of Zn-NC in the early stages is wider than that in the later stages. Diffraction peaks at 4.6 and 6.8° originated from the residue of the SDS surfactant. We could not assign smaller peaks at 4.1 and 8.4° in the cases of 1, 10, and 20 min.

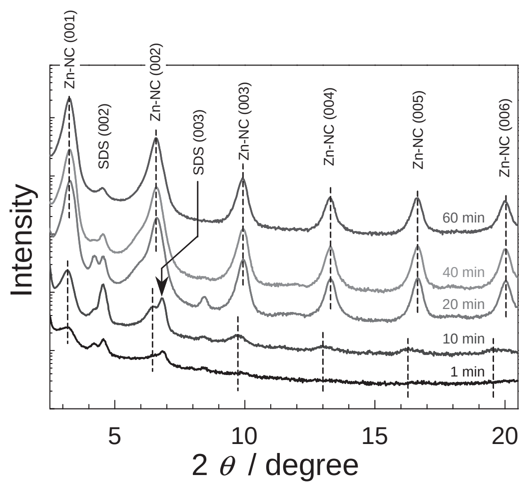

Figure 1. XRD patterns of the products prepared by a laser fluence of 6.7 J/cm^2 for various ablation time.

Figure 2 depicts scanning transmission electron microscopic (STEM) images of the products prepared by 6.7 J/cm^2 for vari-

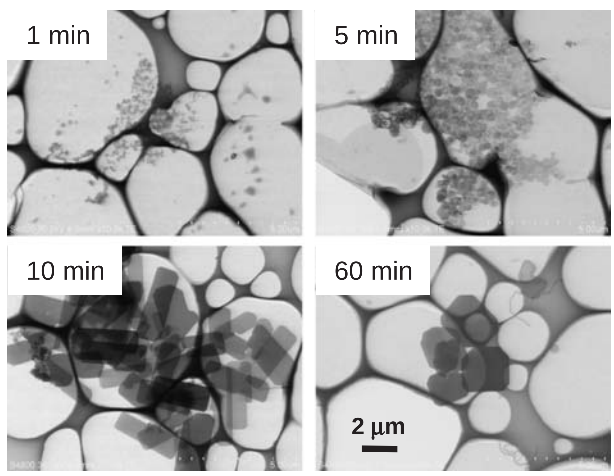

Figure 2. Scanning transmission electron microscopic (STEM) images of the products prepared by a laser fluence of 6.7 J/cm^2 for various ablation time.

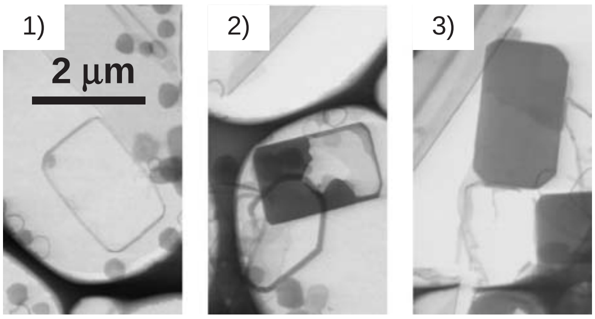

Figure 3. STEM images of the products prepared by a laser fluence of 2.0 J/cm^2 for 60 min.

ous ablation times. At ablation times of 1 and 5 min, platelets with irregular and round shapes were found. These platelets are species of Zn-NC and cannot grow larger crystals because of shorter laser ablation time. Regular octagonal and elongated octagonal shapes of Zn-NC were observed for ablation exceeding 10 min. The regular octagonal shape is the typical morphology of Zn-NC.[3] In contrast, rectangular platelets formed only at 10 min. The SDS monohydrate crystal was reported to have rectangular morphology,[7] which is similar to the Zn-NC produced at 10 min. The rectangular-shaped Zn-NC at 10 min is probably related to the SDS monohydrate.

Figure 3 presents the STEM images of the products prepared by a lower fluence of 2.0 J/cm^2 for 60 min. The products displayed various morphologies, such as small, round platelets, and truncated rectangular structures with different contrast. The lower laser fluence cannot sufficiently supply Zn species, and the Zn-NC formation process terminates halfway. Thus, the obtained morphology reflects the formation process. This figure suggests the following formation process. 1) Small round Zn species and a rectangular shell structure formed first. 2) The shell structure was gradually filled with the Zn species. 3) Filled rectangular Zn-NC was finally obtained.

Crystallized SDS monohydrate forms in an aqueous solution above the critical micelle concentration (CMC) under slow cooling.[7] The concentration of the SDS solution was set to above the CMC in this experiment, and the temperature of the obtained colloidal suspensions decreased to around the Krafft point of 16 °C[8] after the ablation, because the experiments were carried out at room temperature. A similar condition was achieved by laser ablation in the longer ablation time. Thus, platelets of SDS monohydrate crystals could grow in the solution. However, the platelets are composed of Na ions, dodecyl sulfate ions, and water molecules and are transparent and extremely thin. Thus, we cannot find the shape of the platelets without special observation equipment, such as an in situ differential interference phase contrast microscope.[7] The SDS monohydrate serves as a template for the rectangular Zn-NC. Figure 4 illustrates a proposed Zn-NC formation process. First, Zn species are formed by laser ablation of the Zn metal target. The species preferentially attaches to edges of the rectangular templates of the SDS monohydrate as shown in Figure 3 because of lower attachment energies at the edges,[7] leading to the shell structure forming in a rectangular shape. Next, Zn ions intercalate into the SDS monohydrate and replace Na ions by ion exchange. Finally, filled Zn-NC in a rectangular shape is obtained. Four rectangular corners of the shell are slightly truncated, which is different from a regular rectangular shape of SDS monohydrate suggested by theoretical prediction. This implies that the rectangular shape of Zn-NC began to change to octagonal shape before the filling template was over. At the lower laser fluence of 2.0 J/cm^2, the Zn-NC formation proceeded slowly, allowing the formation progress to be observed. In contrast, the formation of rectangular Zn-NC proceeded very quickly at the higher fluence of 6.7 J/cm^2. The Zn-NC can effectively absorb the laser beam of 355 nm because the absorption band exists at 370 nm.[6] The laser irradiation for the rectangular Zn-NC probably leads a photoexcitation and dehydration in the interlayer water molecules. Therefore, the morphology change and the shrinkage of interlayer spacing from the rectangular to octagonal Zn-NC are possibly caused by the dehydration due to laser irradiation for Zn-NC. The elongated octagonal shape of Zn-NC could be a transient shape from truncated rectangular Zn-NC to regular octagonal Zn-NC. The appearance of the additional unknown XRD peaks may be attributed to breaking the symmetry of the crystal structure.

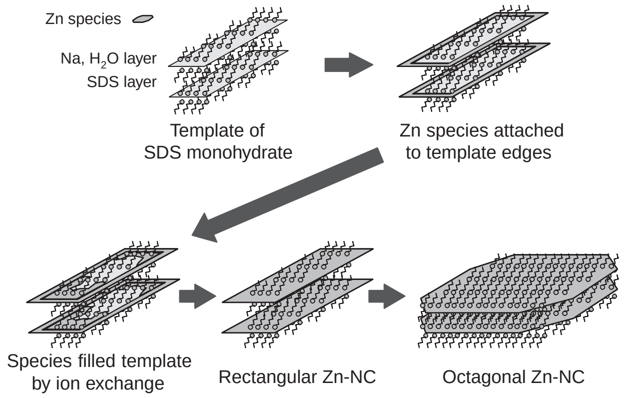

Figure 4. Proposed formation process of Zn-NC.

In summary, layered zinc hydroxide nanocomposites (Zn-NC) were prepared by laser ablation in an aqueous solution of sodium dodecyl sulfate with various ablation times and laser fluences. At a fluence of 6.7 J/cm^2, rectangular Zn-NC was obtained by 10 min ablation, and octagonal Zn-NC was formed by longer ablation time than 10 min. At a fluence of 2.0 J/cm^2, the species of Zn-NC, rectangular shell and filled Zn-NC were produced. These results suggest that SDS monohydrate with a rectangular shape acts as a template in the solution for Zn-NC formation.

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