Effect of Alkyl Chain Length on Layered Structure of Zn Nanocomposites Prepared by Laser Ablation of Zn in Aqueous Solution of Sodium Alkyl Sulfate

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Laser ablation of Zn was performed in aqueous solution of sodium alkyl sulfate ($C_nH_{2n+1}SO_4Na$) with different alkyl chain lengths n. Zn nanocomposites (Zn-NC) with layered structures were obtained at specific alkyl chain lengths ($n = 12$, 13, 14, and 16). The interlayer spacing of Zn-NC and the tilt angle of surfactant molecules in the interlayer increased with alkyl chain length n. The increase in the tilt angle suggests the increase in packing density of surfactant molecules due to strong attraction forces between longer alkyl chains.

Hybrid organic/inorganic nanocomposites composed of Zn and pillared surfactant molecules with two-dimensional (2D) platelet morphology were synthesized by laser ablation of a Zn metal target in an aqueous surfactant solution of sodium dodecyl sulfate (SDS; $C_{12}H_{25}SO_4Na$).[1] 2D sheet materials are attracting great attention because of their nanoscale thickness and high anisotropy, which are suitable for the study of dimensionally confined transport phenomena.[2] However, the detailed structure and formation mechanism of regularly layered Zn nanocomposites (Zn-NC) have not yet been clearly revealed. Zn-NC with different layer spacing is expected to be formed using sodium alkyl sulfate with different chain lengths, which is quite helpful to study the detailed structure and the formation mechanism of the Zn-NC. The photoluminescence is also useful for analyzing the electronic structure of Zn-NC. In this letter, we investigate the effect of the alkyl chain length on the Zn-NC structure and the photoluminescence.

Laser ablation in solution was used to prepare Zn-NC in this study. The solutions used were deionized water and an aqueous surfactant solution of sodium alkyl sulfate $C_nH_{2n+1}SO_4Na$ with different alkyl chain lengths n ($n = 9$–18). The concentrations of aqueous sodium alkyl sulfate solutions were changed from 1×10^{-3} to 1×10^{-1} mol/dm^3 to set the concentration above their critical micelle concentrations (CMCs)[3] because micelle formation of surfactant molecules is supposed to play an important role for layered structures of the nanocomposite. 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 with fluence of 6.7 J/cm^2 irradiated the Zn metal target, which was fixed on the bottom of a glass vessel filled with the solution. Further detailed conditions were described in our previous paper.[4] Colloidal suspensions were obtained after laser ablation for 1 h at room temperature. The suspensions were dropped on a 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. The X-ray diffraction (XRD; Rigaku RAD-C, Cu Kα irradiation) measurements were performed for the precipitates dried on the quartz glass substrates. The photoluminescence spectra of the colloidal suspensions were measured by a fluorophotometer (Shimadzu RF-5300PC) excited at 220 nm (5.64 eV) without a cutoff filter at room temperature.

The XRD results indicated that ZnO formed in deionized water and for $n = 9$, 10, 16, and 18, and that the regularly layered structure of Zn-NC was found for $n = 12$, 13, 14, and 16. No diffraction pattern was found for $n = 11$. Figure 1 depicts scanning transmission electron microscopic (STEM) images of the products prepared in an aqueous solution of sodium alkyl sulfate with different n. The morphology and size of products varied dramatically with n. Polygonal platelet morphology was observed for $n = 12$, 13, 14, and 16, possibly because of the preferential growth orientation of Zn-NC crystal as in the case of SDS hydrate crystal.[5] In contrast, nanoparticles were observed in deionized water and the sodium alkyl sulfate solutions with $n = 9$, 10, and 18. Both Zn-NC and ZnO nanoparticles were obtained when n is 16.

The Zn-NC prepared in SDS ($n = 12$) solution has regularly spaced Zn layers with an interlayer of a tilted tail-to-tail bilayer of dodecyl sulfate molecules.[1] The Zn-NC can be characterized

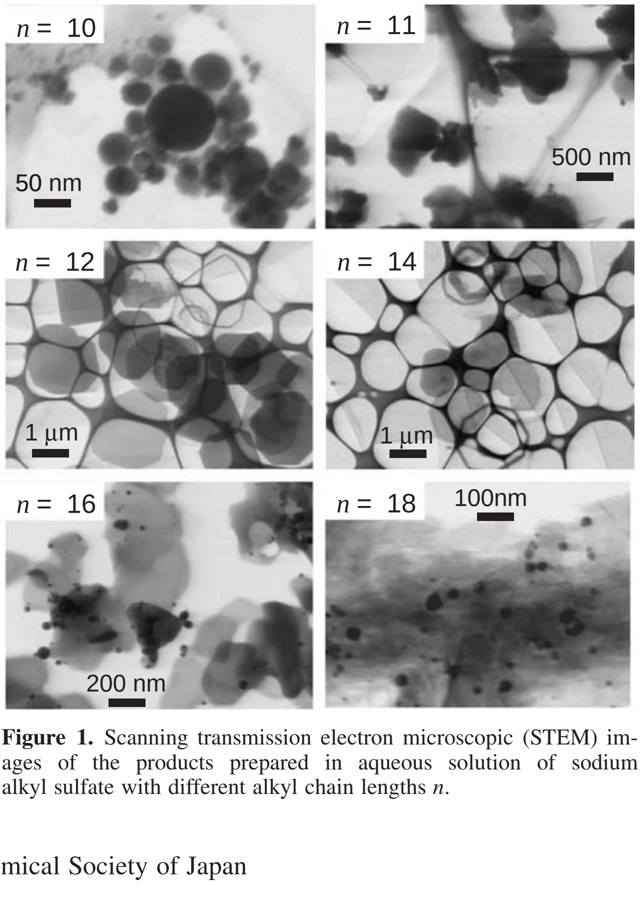

Figure 1. Scanning transmission electron microscopic (STEM) images of the products prepared in aqueous solution of sodium alkyl sulfate with different alkyl chain lengths n.

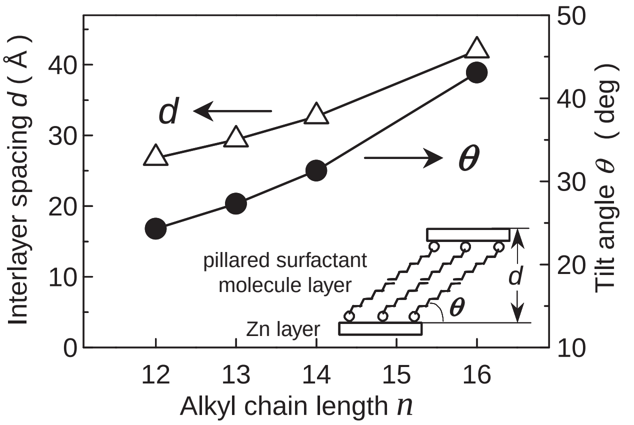

Figure 2. Effect of alkyl chain length n on interlayer spacing and tilt angle of Zn nanocomposites prepared in aqueous solution of sodium alkyl sulfate with $n = 12$, 13, 14, and 16.

by two structural parameters, the interlayer spacing of Zn layers and the tilt angle between the alkyl chain direction of surfactant molecule and the Zn layer plane. The interlayer spacing d was calculated from equally spaced sharp diffraction peaks (00l) at lower angles (3–25°) using the Bragg formula. The tilt angle θ was estimated from a simple geometrical calculation using Zn layer thickness, surfactant molecule length, and sulfate ion size.[3] Figure 2 illustrates the effect of the alkyl chain length n on the interlayer spacing and the tilt angle of Zn-NC. The interlayer spacing and the tilt angle increased with n. A similar experimental result was reported for self-assembled nanocomposite platelets of montmorillonite composed of pillared alkyl ammonium molecules with different alkyl chain lengths.[6] Such n dependency is possibly due to the packing density increase of surfactant molecules in the interlayer produced by the stronger attraction forces of hydrophobic interaction between alkyl chains.[7]

Zn-NC did not form at shorter alkyl chain lengths ($n = 9$, 10, and 11) since the surfactant molecules could not be self-assembled because of their weak attraction forces. In contrast, the surfactant molecules with the longest alkyl chain ($n = 18$) also failed in self-assembling. Over-expanded interlayer spacing due to excessively long chains might provoke exfoliation of layers[7] and destruction of the pillared structure. Thus, the surfactant molecules with $n = 11$, 18 at the boundary between the formation range of nanoparticles and layered structures formed a sheet-like amorphous material as observed by FE-SEM. Consequently, a specific alkyl chain length ($n = 12$–16) is necessary for the formation of Zn-NC with the regularly layered structure.

Figure 3 presents photoluminescence spectra of the colloidal suspensions of ZnO nanoparticles and Zn-NC prepared in an aqueous solution of sodium alkyl sulfate with different alkyl chain lengths n. The UV emission peaks were observed for all the cases at around 3.36 eV. The emission peaks are attributed to neutral donor-bound excitons of ZnO.[8] The emission intensities of Zn-NC ($n = 12$, 14, and 16) exceeded those of ZnO nanoparticles ($n = 10$, 18), which may be due to the amplification of multiple light scattering by the micrometer sized Zn-NC platelets. No remarkable influence of n on the spectrum shape and the peak position was found. These results imply that the Zn layer between the pillared surfactant molecule layers could have the same electronic and crystal structure as that of ZnO. No green emission around 2.3 eV due to oxygen defects in ZnO was found in any suspension except for the ZnO nanoparticle suspension prepared in deionized water. This is attributed to passivation of lattice defects in ZnO by surfactant molecules.[4,9]

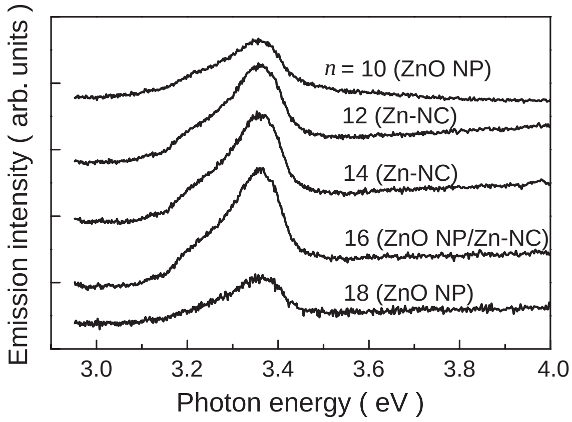

Figure 3. Photoluminescence spectra of colloidal suspensions of ZnO nanoparticles (ZnO NP) and Zn-NC prepared in aqueous solution of sodium alkyl sulfate with different alkyl chain length n.

In summary, Zn-NC with layered structures were prepared by laser ablation in an aqueous solution of sodium alkyl sulfate with different alkyl chain lengths n. The effects of alkyl chain lengths on the Zn-NC structure and the photoluminescence were investigated. Zn-NC was obtained at specific alkyl chain lengths ($n = 12$–16). The interlayer spacing of the Zn-NC and the tilt angle of surfactant molecules increased with n within this chain length range. This is due to the increased packing density of interlayer surfactant molecules caused by the stronger attraction forces within longer alkyl chains. Strong UV emission was observed from the Zn-NC irrespective of the alkyl chain length. This indicates that the Zn layer sandwiched by the pillared surfactant molecule layers could probably have the same electronic and crystal structure as that of ZnO nanoparticles, and the Zn-NC structure strongly depends on the morphology of surfactant molecules in the interlayer.

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