Platelike Crystal Growth of Zn–Al Layered Double Hydroxide by Hot Water Treatment of Sol–Gel Derived Al_2O_3–ZnO Films on Glass Substrate

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We have successfully immobilized Zn–Al layered double hydroxide (LDH) directly on glass substrates through the sol–gel method with hot water treatment. Al_2O_3–ZnO thin films were originally prepared on glass substrates by the sol–gel method with a heat treatment at 400 °C for 30 min, and then the films were immersed in distilled water at 100 °C for 15 min to form nanocrystalline Zn–Al LDH with hexagonal structure.

The control of surface structure of thin films is very important because fine surface structure in nanoorder size brings various superior properties to the films. We have investigated the surface structure of sol–gel derived oxide films immersed in hot water[1–6] in order to control the surface structure, and demonstrated a variety of applications of those Al_2O_3 transparent films such as superhydrophilic and superhydrophobic transparent films and anti-reflective films.[2–6] From a viewpoint of expansion in application, we have tried to obtain a variety of surface structure of thin films by using Al_2O_3-based binary oxide systems as well as simple oxides. As the preliminary experiment, we have investigated surface morphology of sol–gel derived Al_2O_3-based binary oxide thin films such as Al_2O_3–M_xO_y (M = Ti, Si, and Zn) through hot water treatment. It was found that surface structure of the films treated with hot water was quite different and it strongly depends on the systems. We have happened to discover that nanocrystals with hexagonal structure were formed on the sol–gel derived Al_2O_3–ZnO thin films on substrates and the obtained nanocrystals were Zn–Al layered double hydroxide (LDH). LDHs consists of positively charged brucite-like $Mg(OH)_2$ sheets with intercalated compensation anions and water molecules, as shown in Figure 1. LDH, which is usually prepared through the coprecipitation process,[7] has been studied as anion-exchangers, catalysts, electrochemical sensors, and the immobilization hosts of biological materials by intercalation of various anions into layers.[7–11]

The present paper reports the formation of the unique surface structure of the LDH precipitated films in the system Al_2O_3–ZnO, which is very different from flowerlike alumina. We believe that the direct immobilization of Zn–Al LDH nanocrystals on glass surface by this process will open new application fields of LDH.

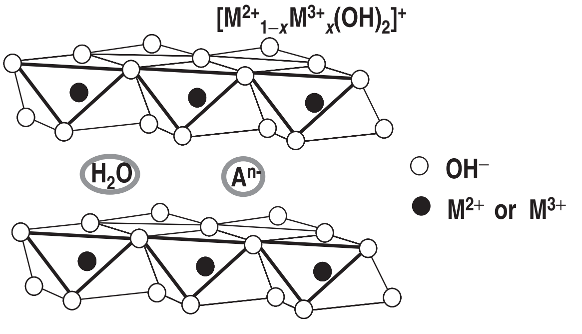

Figure 1. Schematic representation of the LDH.

LDH immobilized thin films were prepared from aluminum tri-*sec*-butoxide ($Al(O\text{-}sec\text{-}Bu)_3$) and zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$) according to the following procedure; $Al(O\text{-}sec\text{-}Bu)_3$, ethyl acetoacetate (EAcAc), and isopropyl alcohol (*i*-PrOH) were mixed and stirred at room temperature for 3 h. A mixture of water and *i*-PrOH was then added dropwise to the solution for hydrolysis. Separately, $Zn(OAc)_2 \cdot 2H_2O$, diethanolamine (DEA), and *i*-PrOH were mixed and stirred at room temperature for 3 h. A mixture of water and *i*-PrOH was added dropwise to the solution. Then, the two solutions were mixed together and stirred at room temperature for 1 h; the obtained solution was used for coating. The molar ratios of $Zn(OAc)_2 \cdot 2H_2O$, *i*-PrOH, EAcAc, H_2O, and DEA to $Al(O\text{-}sec\text{-}Bu)_3$ were 1, 40, 1, 2, and 1, respectively.

The coating of soda-lime silica glass plates was conducted by dip-coating; withdrawal speed was 3 mm/s. The coating films obtained were heat-treated at 400 °C for 30 min to obtain porous Al_2O_3–ZnO films. The Al_2O_3–ZnO films were then immersed in boiling water for 5 s to 3 h and dried at 50 °C for overnight.

The surface and the cross section of the coating films were examined by using field emission type scanning electron microscopy (FE-SEM, Hitachi S-4500). X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 1100 X-ray diffractomater using conventional θ–2θ scan.

The Al_2O_3–ZnO films with the atomic ratio Al/Zn of unity, which were originally transparent, became opaque after the hot water treatment for more than 15 min. Figure 1 shows FE-SEM images of the surface of the Al_2O_3–ZnO films, heat-treated at 400 °C and immersed in hot water for various periods of time. Before the hot water treatment, the surface of the film is smooth as shown in Figure 2a. The film thickness is approximately 100 nm. As shown in Figure 2b, the small roughness begins to form with immersion for only 5 s, and as the hot water treatment time becomes long, nanocrystals with hexagonal structure are formed (Figures 2c–2f). It is thought that the nanocrystals were large enough to cause the scattering of the visible light, and the film turned opaque after the hot water treatment. Figure 2g shows the 20 degree slanted cross section of the film after the hot water treatment for 15 min. As it can be observed, nanocrystals with hexagonal structure are formed directly on the substrate, and the thickness is about 500 nm. This is in striking contrast to the pure Al_2O_3 films, on which the flowerlike structure of the size of less than 100 nm is formed. The platelike crystals usually have a trend to grow parallel to the substrates. However, in this case, the layered plane is not parallel to the substrate. If the Al and Zn sources are originally dissolved in the solution, plate-

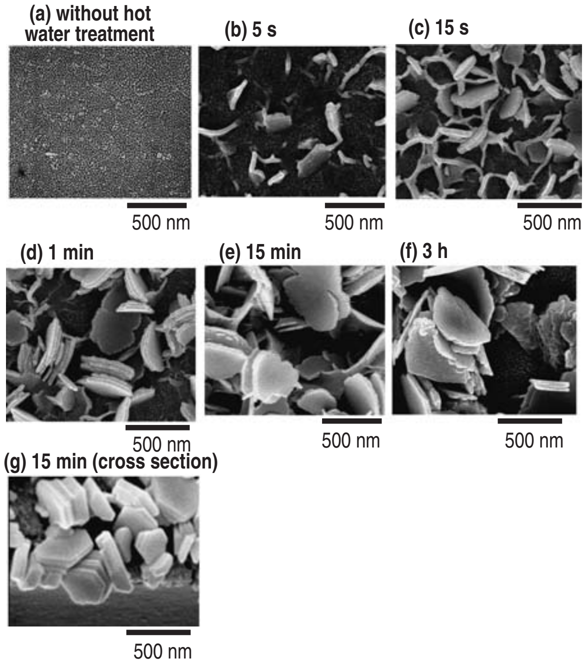

Figure 2. FE-SEM micrographs of the surface of Al_2O_3–ZnO film (Al/Zn = 1) coated on soda-lime glass substrates, and heated at 400 °C; (a), and immersed in boiling water for, (b) 5 s, (c) 15 s, (d) 1 min, (e) 15 min, (f) 3 h, and (g) 20 degree slanted cross section of the film immersed in boiling water for 15 min.

like crystals should have a trend to grow parallel to the substrate. In this case, however, during immersion of the film in hot water, the Al and Zn sources seem to be dissolved from the film on the substrate, and then the ion species immediately diffuse and nucleate at the surface of the film. The nanocrystals are thought to grow by dissolution–reprecipitation process, and thus the nanocrystals are not parallel to the substrate in this study. After the hot water treatment for 3 h, the number of crystals is decreased, and as shown in Figure 2f nanocrystals with hexagonal structure are assumed to be flaked away because of overgrown structure, bubble of boiling water, and so on.

The XRD patterns of the film with the atomic ratio Al/Zn of unity are shown in Figure 3. A peak, from which the basal spacing calculated is 0.747 nm, was observed after hot water treatment only for 5 s (b). The observed basal spacing almost agree with the spacing of Zn–Al LDH intercalated with carbonate ions.[10] The intensity of the peak increases with an increase in hot water treatment time, and two sharp peaks were observed after 15 min (d). Consequently, the nanocrystals with hexagonal structure formed on Al_2O_3–ZnO films are Zn–Al LDH. To the best of our knowledge, this is the first case that Zn–Al LDH precipitated films were successfully synthesized directly on glass substrates through the sol–gel method with the hot water treatment, meaning that the simple process can achieve the immobilization of Zn–Al LDH.

In the pure Al_2O_3 system, sol–gel derived porous Al_2O_3 films reacted with H_2O, and the flowerlike structures, which consisted of pseudoboehmite, were formed with the dissolution–reprecipitation process. The nanocrystals formed with the hot water treatment in this study are not boehmite but Zn–Al LDH. This process appears to be similar to the calcination–rehydration process, which is known as a method to obtain LDH intercalated with various organic anions.[7,9–11] In the calcinations–rehydration process, the precursor LDH powder is usually calcinated until the elimination of the interlamellar anion. Then, the calcined product is put in contact with a solution of the desired anion, and the lamellar structure is then reconstructed, with the concomitant intercalation of the selected anion. This phenomenon is called "memory effect."[9–11] On the other hand, in this study Zn–Al LDH is not thought to be reconstructed like memory effect, but newly constructed during the hot water treatment through the dissolution–reprecipitation process.

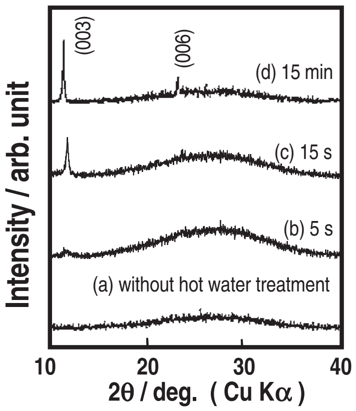

Figure 3. XRD patterns of Al_2O_3–ZnO films (Al/Zn = 1) heated at 400 °C; (a), and immersed in boiling water for, (b) 5 s, (c) 15 s, and (d) 15 min.

Immobilization of LDH nanocrystals on substrates should also be useful to evaluate the intercalation reaction of LDH. The immobilization of the LDH crystals prepared by the coprecipitation has been investigated only by adsorbing the powder on substrates,[12,13] despite the fact that the immobilization of LDHs must be effective to expand the application of LDHs and useful to investigate their formation process. The preparation procedure of LDH thin film on glass substrate as developed in the present study is very simple and will be widely applicable for investigation of LDH in many ways.

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