Preparation of Titania Nanotube Thin Films by Langmuir–Blodgett Technique

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Preparation of thin titania nanotube films has been attempted using Langmuir–Blodgett (LB) technique. The resulting LB monolayer exhibited closely packed arrangement of the nanotube bundles in a monoparticulate layer on the solid substrate. Also, domain structure due to strong lateral interaction among the bundles lying side-by-side was observed even for the LB films deposited at a low surface pressure. Moreover, multilayer deposition of the monoparticulate films provided precise control of the film thickness.

Among various nanoscale tubular metal oxides, titania nanotube has potential applications to dye-sensitized solar cells,[1] photocatalysts,[2–5] sensors,[6–8] and semiconductor devices.[9] Since the work of Kasuga et al.,[10] a hydrothermal alkaline treatment of crystalline TiO_2 has been widely used to fabricate titania nanotubes as an alternative to templating method. While composition, thermal stability, and formation mechanism of the titania nanotubes prepared by hydrothermal treatment of TiO_2 powder are still being debated in recent years,[2,11–20] they are of great interest for the low crystallinity, large surface area,[21,22] and scroll structure.[14–16]

When inorganic tubular particles are utilized as a surface modifier or an electrode material, they are generally immobilized on the substrate surface to form thin layer. In order to take advantage of peculiarity of the nanotube morphology, film structure, e.g., packing and orientation of nanotubes as well as deposited amount of particles would be crucial. On the other hand, Langmuir–Blodgett (LB) technique offers precise control of the layer structure not only for organized molecular films but also for inorganic particulate films.[23] Such a well-defined film structure would be appropriate for studying characteristics of the films quantitatively. In the present work, we attempted to fabricate thin titania nanotube films on the solid substrates by means of LB technique and examined the structure of the particulate films.

All chemicals except anatase-type TiO_2 sol (Taki Chemical Co., Ltd.) and cetylammonium chloride (Lion Co., Ltd.) were commercially available. These materials were of the highest grade and used without further purification. Titania nanotubes were prepared by hydrothermal treatment of the TiO_2 sol with 10 M NaOH for 24 h at 150 °C in a stirred autoclave. After the hydrothermal treatment, the crude product was suspended in distilled water and filtered to remove NaOH from the solution. This purification procedure was repeated until the pH of the filtrate reached almost neutral. To fabricate titania nanotube films, LB technique was applied to the deposition process as follows: first, titania nanotubes in the aqueous dispersion were hydrophobized by treatment with cetylammonium chloride. Next, the nanotubes were extracted with benzene and were spread from the benzene dispersion on the surface of distilled water. The floating nanotubes were compressed at 1–18 $mN\,m^{-1}$, followed by LB deposition on the solid substrate by vertical dipping method at 20 °C. Surface morphology and structure of the LB films were observed by a Hitachi S-4100 scanning electron microscope (SEM). UV–vis absorption spectra and ζ-potential were measured with a Shimadzu UV-3100PC UV–vis–near-IR scanning spectrophotometer and an Otuka Electronics ELS-800 electrophoretic light scattering spectrophotometer, respectively.

Figure 1 shows SEM image of prepared titania nanotubes casted on the glass substrate. The nanotubes tended to form aggregated bundles with length of several µm. They are randomly intertwined with each other forming network-like structure. Mean diameter of the tube bundles is estimated to be ca. 45 nm, though the diameter values are somewhat distributed depending on the number of tubes in a bundle. Taking into account that the diameter of the single titania nanotube is 7–12 nm,[2,3,11–14,22] the bundles are considered to be made up of 10–15 tubes in average. To study the surface electrical properties of the titania nanotubes in the aqueous dispersion, ζ-potential was measured as a function of pH. As a result, it was found that the nanotubes have negative surface charge in a wide pH range (pH 4–13). A negative maximum of -60 mV appeared at around neutral pH. Accordingly, cationic surfactant is expected to adsorb strongly to the nanotube surface by Coulombic interaction. In fact, the treatment with cetylammonium chloride makes the titania nanotubes so hydrophobic that the nanotube bundles spread on the distilled water were stable enough to keep the Langmuir monolayer in compressing process.

SEM images of the titania nanotube LB films (monolayer) deposited at various surface pressures are shown in Figure 2. For the LB film at low surface pressure of 1 $mN\,m^{-1}$, tube bundles spontaneously form islands in a side-by-side arrangement. This indicates that the lateral interaction acts most sufficiently among rod-like particles aligned parallel to each other at the surface of subphase. These islands are gathered as the surface pressure increases, and a densely packed monoparticulate layer is formed above 10 $mN\,m^{-1}$. As shown in Figure 2b, the titania

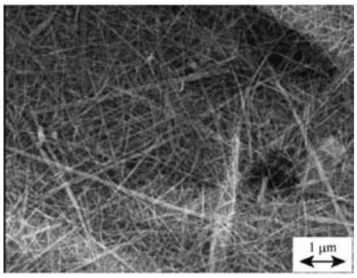

Figure 1. SEM image of titania nanotubes prepared from TiO_2 sol with 10 M NaOH for 24 h at 150 °C.

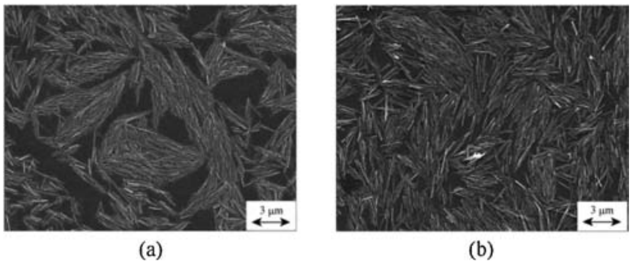

Figure 2. SEM images of titania nanotube LB films (monolayer): surface pressure; (a) $1\,\mathrm{mN\,m^{-1}}$, (b) $18\,\mathrm{mN\,m^{-1}}$.

nanotube bundles are deposited like floating logs and they uniformly cover the substrate surface. Also, the assembled islands form domain structure (domain size: 5–10 μm). Unlike the case of the cast film in Figure 1, all particles are arranged in lie-flat orientation and little overlap is presented in these images. From these results, we can conclude that the monoparticulate layer of the titania nanotube bundles is successfully deposited by the LB technique. In addition, compared to the as-prepared nanotubes in Figure 1, length of the bundles in the LB films seemed to be shortened to a few μm probably because of some mechanical damage through purification and deposition processes.

Furthermore, in order to control the film thickness, we carried out multilayer deposition of the monolayers at a surface pressure of $18\,\mathrm{mN\,m^{-1}}$. In this process, it was observed that the floating particulate monolayer is transferred only in the upstroke direction of the substrate. Also, sufficient drying time was required between dips to prevent respreading of the deposited layer during downstroke of the substrate. Figure 3 shows UV–vis absorption spectra of the 1–4-layer LB films. The inset figure plotting absorbance at 280 nm against the number of layers indicates the proportional relationship between them; therefore, it is clear that uniform and regular deposition of the particulate films can be achieved by the LB technique. This means that the film thickness could be precisely controlled by the deposition time. Figure 4 shows the surface morphologies of the 4-layer LB films. In this figure, the titania nanotube bundles are arranged two-dimensionally in the respective layers, showing a texture of piled up rod-like particulate monolayers. Taking into account the mean diameter of nanotube bundle to be 45 nm, the thickness of the 4-layer film is expected to be less than 0.2 μm. In addition, defects are sparsely observed in the 4-layer LB film (Figure 4b). Since the ruptured films are strong enough to form the walls of cavities though they consist of two or three layers (we can see the bottom layer inside of the cavities), the strength of the film is considered to increase drastically with increasing number of layers. Such a self-standing property would be attributed to the piled up rod-like particulate monolayers, i.e., domains with the oriented titania nanotube bundles in the each neighboring monoparticulate layer act as warp and weft, reinforcing the film in two-dimensional direction.

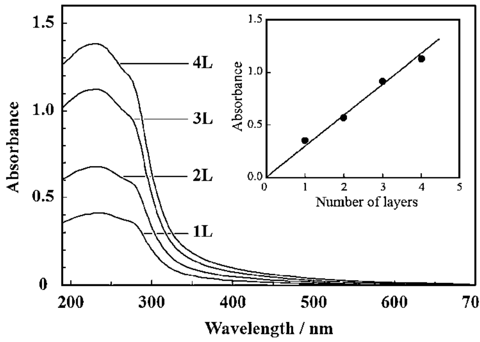

Figure 3. UV–vis absorption spectra of titania nanotube LB films (1–4 layers). The inset indicates the plots of absorbance at 280 nm vs. number of deposited layers.

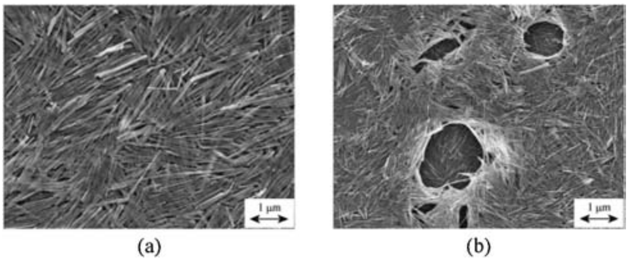

Figure 4. SEM images of the 4-layer titania nanotube LB film.

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