Fine Structure of Multi-particle Layered Organization for Organo-modified Zirconium Dioxides Fabricated by the Langmuir-Blodgett Technique

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Formation and structure of organo-modified zirconium dioxides of multi-particle layered organization were investigated by out-of plane and in-plane X-ray diffraction (XRD) and atomic force microscopy (AFM). The surface modification of zirconia particle was performed by several long-chain carboxylic acids with different lengths. Langmuir monolayers of these particles were extremely condensed on the water surface. Multi-particle layered organization was constructed by the Langmuir-Blodgett (LB) technique. From the results of out-of plane XRD measurement of the multilayers of oleic acid-modified ZrO₂ particles, a sharp peak was clearly observed at 52 Å. AFM image at mesoscopic scales of this single particle layer show particle assembly at 50 nm diameters. However, fine particles at about 5 nm diameters are confirmed in the case of high-resolution AFM observation to the mono-particle films transferred at low surface pressure region. Therefore, it is found that regular periodic structure along the c-axis and a hierarchical aggregated particle form were fabricated by Langmuir and LB technique.

Key words: Organo-modification, Langmuir-Blodgett Film, Layered Organization, Zirconium dioxide, Molecular Arrangement

1. INTRODUCTION

Two-dimensional integration of nano-particles has played important roles in the modern technology. This method have received considerable attention because of their potential use in numerous technical applications, ranging from several organic devices to biological materials.¹ On the other hand, organic/inorganic hybrid materials have attracted much attention from both scientists and engineers owing to their remarkable enhancement in dimensional stability, gas-barrier performance, in addition to mechanical properties as compared with conventional composite materials.² Further, many researchers have also attempted to utilize zirconia (zirconium dioxide; ZrO₂) such as imitation diamond, pigment, and fuel cell because ZrO₂ exhibits high refractive index, high band gap, ion conductivity.³ Therefore, attainment of two-dimensional integration of ZrO₂ is possible to enhance several material functionalities. However, it is difficult to obtain regular arrangement of ZrO₂ particles since van der Waals interaction between inorganic materials relatively weak. Surface modification by organic compounds to the inorganic ones is efficient to increase affinity between particles. Previously, we have investigated formation and structure of organized molecular films of organo-modified clay.⁴ In this case, this organo-modified inorganic material formed extremely condensed monolayer on the water surface. Further, highly order layer structure along the c-axis and two-dimensional packing in ab-plane were commonly constructed.

In the present study, floating monolayers and ultra-thin films on solid of organo-modified ZrO₂ were constructed by the Langmuir-Blodgett (LB) technique. These LB multilayers of organo-modified ZrO₂ were characterized by the out-of-plane and in-plane X-ray diffraction (XRD), glazing incidence small angle X-ray scattering (GI-SAXS), and atomic force microscopic (AFM) observation.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Synthesis of organo-modified zirconia (Fig. 1) Dispersed solution is prepared by ZrO₂ aqueous solution and methanol containing long-chain carboxylic acid. Toluene was poured into dispersed solution with stirring. In this step, dispersed solution with stirring. In this step, Figure 1. Formation process of organo-modified ZrO₂: ⁵ organo-modified ZrO₂ migrates from dispersion.

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2.1 Formation of monolayers on water surface and observation of molecular arrangement in the films.

The packing modes of neat ZrO$_2$ and organo-modified ZrO$_2$ were examined using wide-angle X-ray diffraction (WAXD) instrument (Rigaku, R-axis Rapid, CuK$\alpha$ radiation, 40 kV, 200 mA) which was equipped with a graphite monochromator. The layer structures of the comb copolymers were characterized using grazing-incidence small-angle X-ray scattering (SAXS) instrument (Rigaku, Nano-viewer, CuK$\alpha$ radiation, 40 kV, 30 mA).

2.2 Structural analysis in bulk.

The surface morphologies of the transferred films were observed using a scanning probe microscope (Seiko Instrument, SPA300 with SPI-3800 probe station) and microfabricated rectangular Si cantilevers with integrated pyramidal tips by applying a constant force of 1.4 Nm$^{-1}$. The large spacing between the layer structures of the films transferred onto the glass substrates were measured using an out-of-plane X-ray diffractometer (Rigaku, USI-3-22 Teflon-coated LB trough).

2.3 Formation of monolayers on water surface and observation of molecular arrangement in the films.

Monolayers of organo-modified ZrO$_2$ were formed by spreading a chloroform solution (ca. $1.0 \times 10^{-3}$ M) onto a distilled water (18.2 MΩ·cm). After the evaporation of chloroform for 5 min, the surface pressure-area (π-A) isotherms were recorded at a compression speed of 0.08 mm sec$^{-1}$. The air-water interface was kept at a constant temperature of 15 °C by circulating thermostatic water around the trough. The measurements of the monolayer properties and LB film-transfer were carried out using a USI-3-22 Teflon-coated LB trough (USI Instruments).

Figure 2 Out-of plane XRD profiles of LB multilayers of (a) stearic, (b) oleic (c) lauric, (d) octanoic, (e) hexanoic, (f) butanoic acid-modified ZrO$_2$. Figure 3 In-plane XRD profiles of LB multilayers of (a) stearic, (b) oleic (c) lauric, (d) octanoic, (e) hexanoic, (f) butanoic acid-modified ZrO$_2$. Figure 4 Schematic illustration of packing mode of organo-modified ZrO$_2$ in LB film estimated by in-plane XRD and WAXD.

Figure 5 GI-SAXS profiles of LB multilayers of (a) stearic, (b) oleic (c) lauric, (d) octanoic, (e) hexanoic, (f) butanoic acid-modified ZrO$_2$. The measurements of the monolayer properties and LB film-transfer were carried out using a USI-3-22 Teflon-coated LB trough (USI Instruments).
Rint2-Ultima III, CuKα radiation, 40 kV, 40 mA) equipped with a graphite monochromator. The in-plane spacing of the two-dimensional lattice of the films was determined using an X-ray diffractometer with different geometrical arrangements\(^6,\!^7\) (Bruker AXS, MXP-BX, CuKα radiation, 40 kV, 40 mA, an instrument specially made to order) and equipped with a parabolic graded multilayer mirror. The X-rays were incident at an angle of 0.2°, and the films were slow scanned at a speed of 0.05°/80 s; thus, in-plane XRD measurements were carried out at a monomolecular resolution.

### 3. RESULTS AND DISCUSSION

Single particle layers on the water surface of organo-modified ZrO\(_2\) formed extremely condensed films. These films transferred on solid substrate by LB method. Figure 2 shows out-of plane XRD profiles of LB multilayers of organo-modified ZrO\(_2\). It is found that modification by relatively longer alkylated acid formed ordered layer structure in their LB films. That is to say, stearic, oleic, lauric, octanoic acid-modified ZrO\(_2\) have regular arrangement along the c-axis.

Figure 6 Guinier plots of GI-SAXS data and paracrystal analysis of out-of plane XRD data of LB multilayers as calculation of several structural parameters.

Into particles is shown at wide angle side. Figure 4 shows schematic illustration of packing modes of organo-modified ZrO\(_2\) in LB film estimated by in-plane XRD and WAXD. Crystal structure in particle corresponds to monoclinic system. On the other hand, packing of particle itself is two-dimensional hexagonal form. Further, Guinier plots\(^8\) are obtained by GI-SAXS data. From the result of Guinier plots, minimum diameters of particles correspond to 5.6 nm. In addition, three dimensional paracrystal analysis\(^9\) performed by result of out-of plane XRD. In this case, distorted value is 0.5. This result is almost corresponding to 50 % crystalline regularity of

![High resolution AFM images of single particle layer of organo-modified ZrO\(_2\).](image)

![Mesoscopic AFM images and schematic illustration of single particle layer of organo-modified ZrO\(_2\).](image)

![Film thickness vs. transmittance of of LB multilayers of organo-modified ZrO\(_2\).](image)
multi-particle film. Figure 7 shows high resolution AFM image of single particle layer of stearic acid-modified ZrO$_2$. This sample transferred at 1.0 mN m$^{-1}$ from distilled water. The isolated particle sizes were almost 6.0 nm. Figure 8 shows mesoscopic AFM images and schematic illustration of single particle layers of stearic acid-modified ZrO$_2$. AFM images imply formation of a hierarchical particle aggregated structure in two kinds of different parts of the film surface. The images at 4 x 4 $\mu$m$^2$ indicate that “apparent” single particle layer at about 200 nm diameters is formed. Indeed, these “apparent” single particles are composed of fine ones at about 5-6 nm diameters from the results of 1 x 1 $\mu$m$^2$ scale images. This result is well-corresponding to high resolution AFM image. This hierarchical structural formation was summarized in illustrations. Figure 9 shows film thickness vs. transmittance of LB multilayers of organo-modified ZrO$_2$. Wavelength of transmission light corresponds to 500 nm in this measurement. Values of transmittance of Lauric and oleic acid-modified materials are 75 and 40 %, respectively. On the other hand LB multilayers of stearic acid-modified ZrO$_2$ indicate the value of transmittance 10 % at 60 nm film thickness. This result implies the construction of ultra-thin non-transparent film.

4. CONCLUSIONS

We investigated formation and structure of single and multi-particle layers for organo-modified ZrO$_2$. Langmuir monolayer of organo-modified ZrO$_2$ extremely condensed on the water surface. Multi-particle layered organization constructed by the LB technique. From the results of out-of plane XRD measurement to the multilayers for oleic acid-modified ZrO$_2$ particles, a sharp peak was clearly observed at 52 Å. AFM image at mesoscopic scales of this single particle layer show particle assembly at 20-50 nm diameters. However, fine particles at about 5 nm diameters are confirmed in the case of high-resolution AFM observation to the mono-particle films transferred at low surface pressure region. Therefore, it is found that regular periodic structure along the c-axis and a hierarchical aggregated particle form were fabricated by Langmuir and LB technique.

5. REFERENCE


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