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Formation and structure of fine multi-particle layered organo-modified zirconium dioxides fabricated by Langmuir–Blodgett technique

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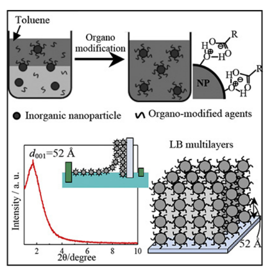
HIGHLIGHTS

- A periodic structure and hierarchical aggregated particle are fabricated by LB techniques.
- The surface modification of zirconia particles is possible to perform using several fatty acids of different lengths.
- It is possible to uniformly disperse organo-ZrO_2 as spreading solution of Langmuir monolayer.
- Fine particles of ZrO_2 with ~5 nm diameter are existed in the case of single-particle.
- The layered organization of the organo-nanodiamond was also constructed by LB technique.

GRAPHICAL ABSTRACT



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ABSTRACT

Formation and structure of multilayered organization of organo-modified zirconium dioxide are investigated by surface pressure–area (π–A) isotherms, out-of-plane and in-plane X-ray diffraction (XRD) analysis, and atomic force microscopy (AFM). In this study, solubilization technology of inorganic fine particles into general solvent has proposed and formation technology of highly ordered single-particle layer has also established by using that inorganic solution as "spreading solution" of the interfacial film. The surface modification of zirconia particles is performed using several long-chain carboxylic acids of different lengths. Accordingly, it is easily achieve a regular arrangement of ZrO_2 particles to overcome the relatively weak van der Waals interactions between the inorganic materials. A Langmuir monolayer of these particles is extremely condensed. A multi-particle layered structure is constructed by the Langmuir–Blodgett (LB) technique. The out-of-plane XRD measurement of multilayered organization of stearate-modified ZrO_2 particles confirms sharp peaks at 59 Å. AFM images on a mesoscopic scale of this single-particle layer of stearate-modified ZrO_2 show the aggregate of particles with 50 nm diameters. However, fine particles with ~5 nm diameter are confirmed from high-resolution AFM observations in the case of single-particle layers transferred at low surface pressure. That is to say, a regular periodic structure along the *c*-axis and a hierarchical aggregated particle form are fabricated by Langmuir and LB techniques.

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1. Introduction

Two-dimensional integration of nanoparticles has played an important role in the development of modern technology. These integrated nanoparticles have received considerable attention because of its potential use in numerous technical applications ranging from organic devices to biological materials [1–4]. Organic/inorganic hybrid materials [5,6] have also attracted much attention from scientists as well as engineers owing to the remarkable enhancement in the dimensional stability and gas-barrier performance, in addition to improved mechanical properties compared to conventional composite materials [7,8]. Another material of interest to researchers is zirconia (zirconium dioxide; ZrO_2), which is used in products such as imitation diamonds, pigments, and fuel cells because ZrO_2 exhibits a high refractive index, high band gap, and increased ion conductivity [9–11].

Thus, it is thought that two-dimensional integration of ZrO_2 nanoparticles would make it possible to enhance several material functionalities [12–14]. However, it is difficult to obtain regular arrangements of ZrO_2 particles because van der Waals interaction between the inorganic materials is relatively weak. To overcome this limitation, surface modification by organic compounds is an efficient way to increase the affinity between particles. In a previous study, we investigated the formation and structure of molecular films of organo-modified clay [15,16]. In that study, the organo-modified inorganic material formed an extremely condensed monolayer on the water surface. Further, a highly ordered layer structure along the *c*-axis and two-dimensional packing in the *ab*-plane were commonly constructed by the Langmuir–Blodgett (LB) technique [17,18].

In the present study, ultrathin organo-modified ZrO_2 films were constructed by method of floating Langmuir monolayers. Technique proposed in this study corresponds a nano-dispersed technology of insoluble inorganic particle as if it solubilized in a general organic solvent. This nano-dispersion solution of the inorganic fine particles can be used as a "spreading solvent" of Langmuir monolayers. That is to say, the formation of LB multilayered organization of the inorganic nanoparticles is made possible. These corresponding LB multilayers of organo-modified ZrO_2 films were characterized by 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. Furthermore, we also examined surface modification, formation of single-particle layer on the water surface, and construction of multi-particle layered organization of the nano-diamond (ND) [19–21], conductive zinc oxide (ZnO), and magnetic triiron tetraoxide particles (Fe_3O_4) particles in order to demonstrate the wide scope of application of this organo-modification technique. The establishment of this technique can be expected that new two-dimensional integration technology of insoluble inorganic nanoparticles widely become possible to propose by using simple wet-process.

2. Experimental

2.1. Characterization of neat zirconia particles and synthesis of organo-modified zirconia

Fig. 1(a) shows the powder X-ray diffraction profile of ZrO_2 nano-particle in bulk. According to the powder diffraction file, crystal structure of this ZrO_2 nano-particle is formed monoclinic (Fig. 1(b)) [22,23]. In addition, by means of approximate analysis of Schererr equation using the (1 1 1) reflection as the maximum intensity peak, average particle size of ZrO_2 was calculated to be 3.0–4.5 nm. Fig. 1(c) shows a previously reported transmission electron micrograph of same type ZrO_2 particle [24]. The individual particle size observed in this image is in good agreement with the size calculated by XRD although there are partially aggregated particles in this TEM image.

Fig. 2 shows a schematic of the synthesis process of organo-modified ZrO_2 [25]. A dispersed mixed solution was prepared by

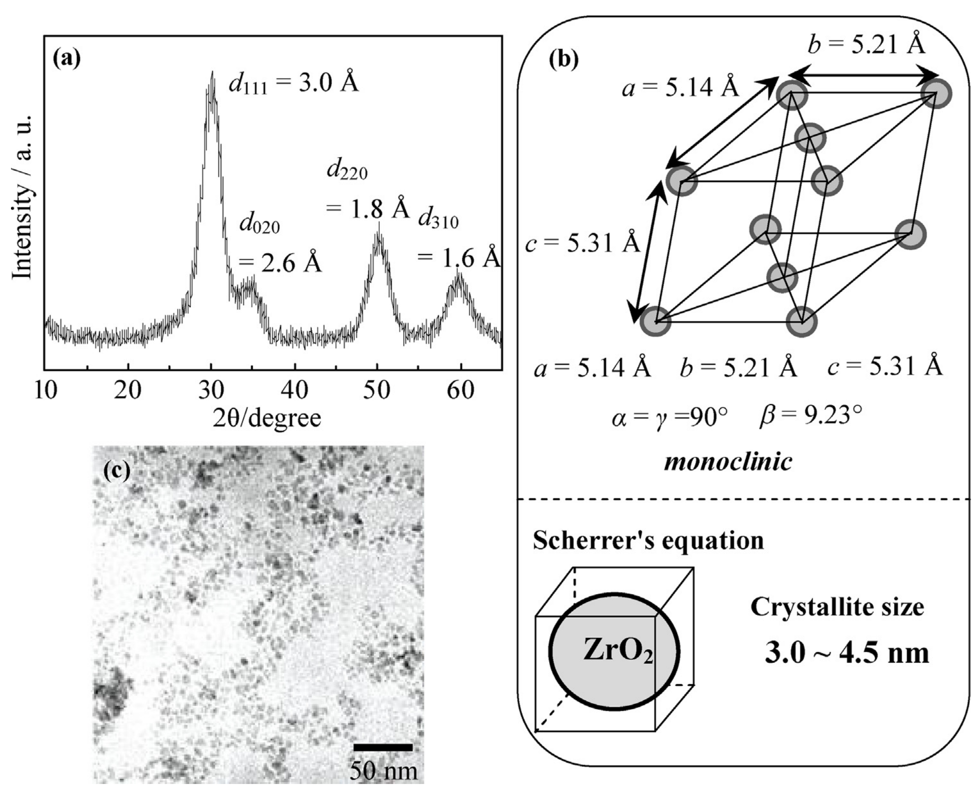

Fig. 1. (a) WAXD profile of ZrO_2 nanoparticle in bulk. (b) Model of crystal lattice and calculation of crystallite size of ZrO_2 [22,23]. (c) TEM image of ZrO_2 particle [24].