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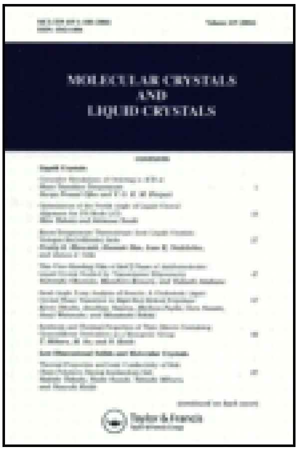

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A Polyoxometalate Multilayer Film by Langmuir-Blodgett Technique

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A Polyoxometalate Multilayer Film by Langmuir-Blodgett Technique

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An organic-inorganic hybrid Langmuir-Blodgett(LB) film was produced through stabilization of a polyoxometalate (POM) monolayer by attaching electrostatically hydrophobic amine (DMDA). The surface pressure-area isotherm of POM-DMDA monolayer showed the stability against surface pressure up to 30 mN/m. The tendency of crystallization on water surface could be directly confirmed by the Brewster angle microscopy. The AFM images showed the aggregated particles of POM-DMDA. The XPS spectra indicated the presence of POM in the LB film and the molecular ratio of DMDA and POM was over 4.0. The XRD spectra showed POMs are positioned to two-dimensionally spread multilayer film..

Keywords: hybrid; polyoxometalate; monolayer; Langmuir-Blodgett; BAM; AFM; XPS

INTRODUCTION

Polyoxometalates (POMs) have potential applications in various fields such as bifunctional catalysis, magnetic nanoparticles, and antiviral and antitumoral chemotherapy[1,2]. Meanwhile, the molecular architectures of organic-inorganic hybrid multilayers have been investigated to produce functional ultrathin films by LB technique[3]. However, POMs have been seldom fabricated into LB films because of their difficulties for synthesis and spreading to monolayers.

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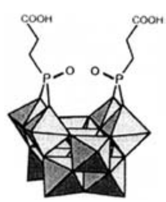
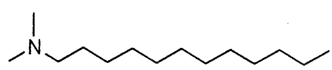
In this paper, we report the organic-inorganic hybrid POM LB film, which was fabricated through stabilization of POM monolayer by introducing hydrophobic alkyl amine. The monolayer on water subphase was evaluated by surface pressure-area (π-A) isotherms and Brewster angle microscopy. The characterization of the hybrid LB film is carried out by FT-IR, XPS, XRD, and AFM.

EXPERIMENTAL

The two carboxyls of POM, $(NBu_4)_3K[\gamma\text{-}SiW_{10}O_{36}(HOOCC_2H_4PO)_2]$, were introduced by phosphonate condensation of $HOOCC_2H_4PO(OH)_2$ with the potassium γ-tungstosilicate. The chemical structure was determined from FT-IR, ^{1}H-NMR, EPR, HR FAB-MS, and elemental analysis.



POM



DMDA

A film balance system NLE-LB200-MWC (Nippon Laser and Electronics) was used for measuring surface pressure as a function of molecular area and for LB transfer of monolayer by the vertical mode (trough surface size, 80x585 mm^2). BAM images were obtained from Mini BAM (Nanofilm Technologie GmbH). The employed substrates were FP-010 filters for XPS, and silicon wafers for XRD, AFM, and FT-IR spectroscopy.

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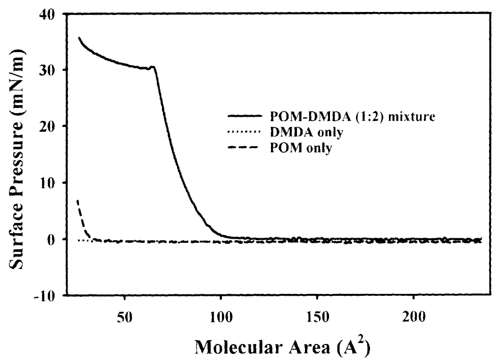

FIGURE 1 Surface pressure-area isotherms of POM and DMDA.

RESULTS AND DISCUSSION

Although the POM itself did not show any development of surface pressure upon monolayer spreading, the surface pressure-area isotherm showed the formation of very stable monolayer on the water subphase when the polyoxometalate was spread together with N,N-dimethyldodecyl amine (DMDA), as shown in Fig.1. The DMDA also did not form the monolayer on water surface by itself. The macroscopic images of the monolayers were monitored by Brewster angle microscopy (BAM). The BAM of POM itself on water surface showed large aggregated images of which molecules are not fully spread to monolayer. The tendency of crystallization on water surface could be directly confirmed by the BAM images. However, the BAM images of POM-DMDA monolayer were not noticeably observed before the monolayer collapse and many dot-like images were seen after the collapse point. The monolayers were transferred on solid substrates as Y type. The hybrid LB films were characterized by XPS and XRD spectra. For quantitative

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analysis, the elemental intensity of W, P, Si, and N atoms was evaluated together with atomic sensitivity factor. The XPS spectra indicated the molecular ratio of DMDA and POM in the LB film was over 4.0. This means that some missing of POM occurred during the monolayer transfer. The XRD spectra showed POMs are positioned to two-dimensionally spread multilayer film. The broadened peaks due to (100), (200), and (300) planes are interpreted as the multilayer film is composed of wavy monolayers. The AFM image of the LB film, which reveals the POMs as aggregated particles, is shown in Figure 2. That is, the POMs are not totally spread to monolayers even in the presence of DMDA molecules.

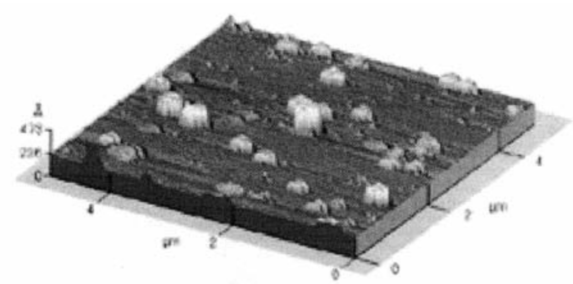

FIGURE 2 AFM image of POM-DMDA LB film.

Acknowledgments.
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