

Orientation Control of Polyoxometalate Nanoparticles in Organic-Inorganic Hybrid LB Films

Burm-Jong Lee*, Hee Sang Kim*, Dong Ho Park*, Sang Hee Nam** and Yunghee Oh***

Abstract - Orientation control of a polyoxometalate (POM) nanoparticle in its two-dimensional arrangement was attempted by Langmuir-Blodgett (LB) technique. For their uniorientation, two carboxyl groups were introduced on one side of the POM particle, and hydrophobic long chains were attached by esterification with the carboxyl groups (C18-POM). The C18-POM layer spread on water surface showed stability against surface pressure up to 60 mN/m. The pattern of the C18-POM isotherm was quite different from stearyl alcohol (C18-OH), while the POM itself did not show any development of surface pressure on water surface. The AFM images of C18-POM LB films showed some microcrystalline structures that were noticed as dot structures by Brewster angle microscopy. The microimages for C18-POM did not completely spread out as a monolayer on the water surface. The XPS spectra indicated the presence of POM structures and stearyl ester bonds formed from about 65% of the total carboxyls. The XRD spectra showed that the unioriented POMs were not positioned with the same lattice distance but rather in a wavy surface state.

Keywords: hybrid, polyoxometalate, monolayer, Langmuir-Blodgett, XRD, BAM, AFM, XPS.

1. Introduction

Polyoxometalates constitute a distinctive class of inorganic compounds, which have been receiving increasing interest over recent years. The structures of polyoxometalates can be described as molecular fragments of close-packed metal oxides with the general formula of $X_aM_bO_c^{n-}$ ($M=Mo, W, V, \dots$ and $X=P, Si, B, \dots$)[1]. The best-known type of polyoxometalates is the Keggin structure, composed of a central heteroatom surrounded by four M_3O_{13} groups ($M=Mo, W$). The polyoxometalates have potential applications in various fields such as bifunctional catalysis, magnetic nanoparticles, energy transfer, luminescence, and antiviral chemotherapy [2, 3]. Recently, Mingotaud *et al.* demonstrated that organic-inorganic ultrathin films containing organized layers of such Keggin polyanions can be readily built by using the Langmuir-Blodgett (LB) technique [4]. We have also reported that a polyoxometalate with carboxyl groups can be fabricated into organic-inorganic hybrid LB films through the electrostatic interaction between oppositely-charged carboxylate-ammonium salt [5]. When the central heteroatom of the Keggin ion has unpaired electronic spins, the built-up films present certain magnetic properties [6]. Meanwhile, Zhang *et al.* has shown effective energy transfer and luminescence

of LB films based on europium-substituted heteropol-ytungstate[7]. Therefore, the polyoxometalates are supposed to be functional nanoparticles by substituting various atoms as component elements.

In this study, we report the possible control of nanoparticle orientation in LB films by attaching long hydrophobic tails as ester bonds to one side of the nanoparticle surfaces. The stability and spreading behavior of the monolayers on water subphase were evaluated by surface pressure-area isotherms and BAM. The chemical and multilayer structures of the hybrid ultrathin films were characterized by XPS and XRD. The surface structure of the LB films was observed by AFM.

2. Experimental

2.1 Synthesis of POM and C18-POM

All the chemicals employed in synthesis were purchased from Aldrich Co. and used without further purification. The two carboxyls of $(NBu_4)_3K[\gamma-SiW_{10}O_{36}(HOCC_2H_4PO)_2]$ (POM) were introduced by phosphonate condensation of $HOCC_2H_4PO(OH)_2$ with the potassium γ -tungstosilicate. The chemical structure was determined from FT-IR, 1H -NMR, EPR, HR FAB-MS, and elemental analysis [3]. POM was subjected to esterification with stearyl alcohol in Dean-Stark apparatus. The structure determination of C18-POM was also performed as described above. Elemental

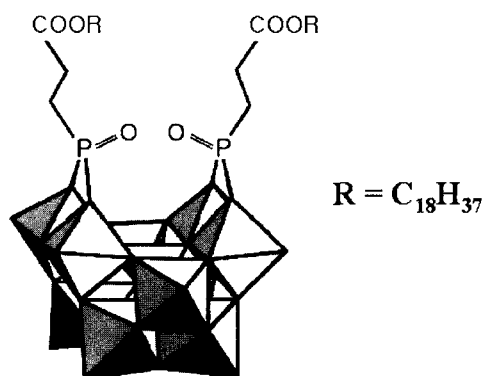
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analysis of C18-POM by XPS revealed that the esterification was not quantitatively carried out. About 65% of the total carboxyl groups were converted to ester bonds. Scheme 1 shows the structure of C18-POM.



C₁₈-Polyoxometalate(C₁₈-POM)

Scheme 1. Schematic structure of C18-POM molecule.

2.2 Characterization of Langmuir monolayer and LB film

A film balance system KSV 2000 system 3 was employed for measuring surface pressure as a function of molecular area and for LB transfer of monolayer by the vertical mode (trough surface size, 960 cm²). The macroscopic images of monolayers on the water surface were monitored from Mini BAM (Nanofilm Technologie GmbH). The employed substrates were FP-010 filters for XPS, and silicon wafers for XRD and AFM. XPS spectra were obtained using an ESCALAB 250 XPS spectrometer (VGI Scientific). The molecular surface morphology of the LB film was scanned by AFM (Nano Scope IV, Digital Instrument). Furthermore, XRD spectra were obtained using the X'PERT-MRD (Philips) model.

3. Results and Discussion

3.1 Characterization of monolayers on water surface

POM itself is an organic-soluble. When the chloroform solution of POM was spread out on the water surface, the POM itself did not show any development of surface pressure even by completed compression of the moving barrier, as shown in Fig. 1 (b). However, the surface pressure-area isotherm showed the formation of a very stable C18-POM layer on the water subphase, i.e., the modification of POM endowing hydrophobic-hydrophilic balance causes C18-POM to form a stable surface layer on the water surface. Although the stearyl alcohol was spread to a monolayer, the monolayer showed a highly condensed

phase, which is quite different from that of C18-POM [Fig. 1 (a) and 1 (c)]. The C18-POM monolayer showed an extremely expanded phase below 20 mN/m of surface pressure and a rather condensed phase by further compression. The limiting area of C18-POM was measured to be about 0.55 nm², which was rather small considering together the counter cations of POMs anion structure.

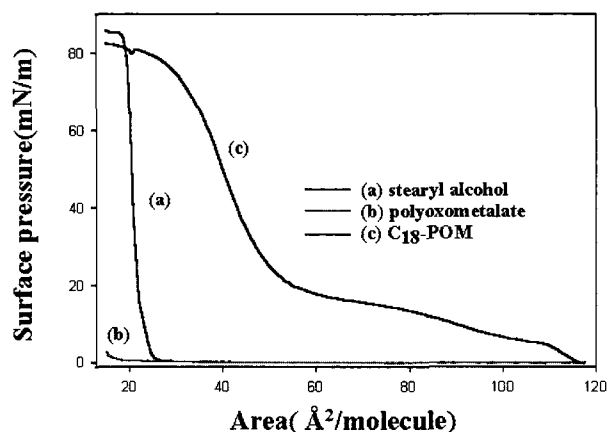


Fig. 1 Surface pressure-area isotherms of C18-POM layer on water surface. The isotherms were obtained by spreading (a) stearyl alcohol, (b) POM, and (c) C18-POM.

The macroscopic images of the monolayers were observed by Brewster angle microscopy (BAM). Fig. 2 shows the BAM images of POM and C18-POM spread on an air-water interface. The BAM images of POM itself on the water surface showed large aggregated structures in which molecules are not thought to be fully spread to a monolayer. The tendency of two-dimensional molecular crystallization on the water surface could be directly confirmed as grafted structures by the BAM images. However, the large collapsed BAM images of C18-POM monolayers were not noticeably observed even after the monolayer collapse.

3.2 Characterization of hybrid C18-POM LB films

The C18-POM monolayers could be transferred on solid substrates, such as Y type. The transfer ratio was in the range of 0.6-0.9 during 20 layer deposition. The hybrid LB films were characterized by XPS and XRD spectra. For quantitative analysis, the elemental intensities of W, P, Si, and N atoms were evaluated together with their atomic sensitivity factors. The XPS spectrum of the C18-POM LB film is shown in Fig. 3. Contrary to the previous dimethyldodecylamine (DMDA)-POM system [5], the XPS spectra of C18-POM indicated less content of C element than expected from C18-POM, of which carboxyls were totally converted with esteric long chain alcohols.

From the results of elemental concentration, we could calculate the esterification ratio of POM with stearyl alcohol to be about 65%. In the case of the DMDA-POM system, the molecular ratio of DMDA and POM in the LB film was found to be approximately 4.0[5].

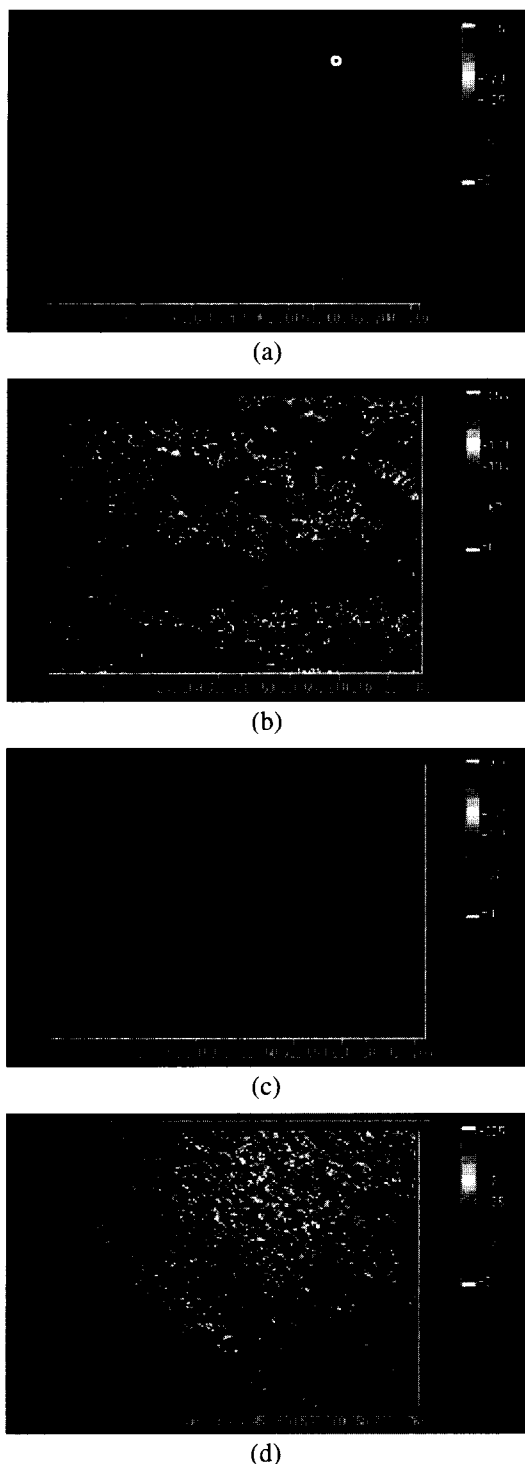


Fig. 2 BAM images of POM and C18-POM. (a) POM as-spread, (b) POM after collapse, (c) C18-POM as-spread, and (d) C18-POM after collapse.

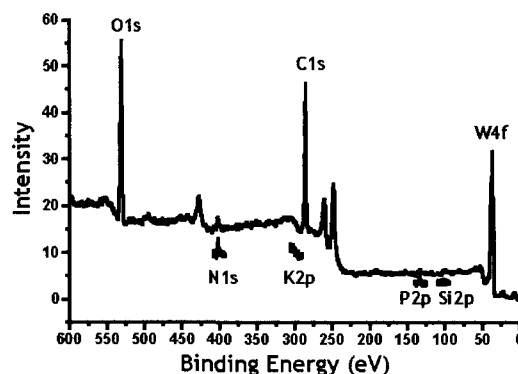


Fig. 3 XPS spectrum of C18-POM LB film deposited 10 layers on FP-010 membrane filter.

The XRD spectra did not show that C18-POM molecules were clearly positioned to a two-dimensionally spread multilayer film. Instead, the spacing between the layers was dependent on the deposited layer numbers as shown in Fig. 4. Three different samples with 31, 21, and 11 deposition layers were respectively examined. In the case of 11 layer LB films, the peaks at 1.57 and 3.09 degrees of 2 theta are correspondent to the d spacing of 5.63 and 2.85 nm, respectively. The 2.85 nm is nearly in agreement with the estimated value of 2.75 nm, which was calculated based on C18-POM with fully stretched chains. The other peaks indicate the LB films contain interdigitated layer structures. The broadened peaks due to (100) and (200) planes were interpreted since the multilayer film was composed of wavy monolayers.

The AFM images of the LB films revealed the C18-POM molecules as aggregated particles as depicted in Fig. 5. That is, the C18-POMs were not completely spread to monolayers even in a very diluted spreading solution. Together with the results of a comparatively small limiting molecular area from surface pressure-area isotherms, the crystalline structures support that the C18-POM was not spread originally to a monolayer on the water surface.

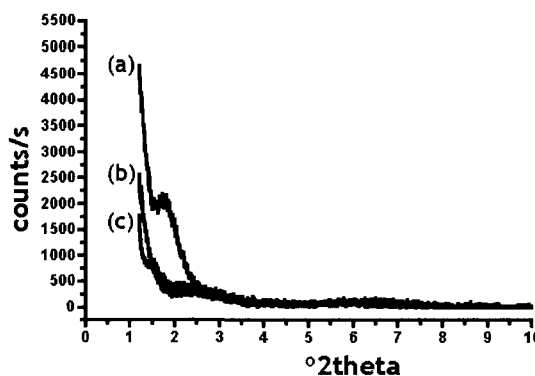


Fig. 4 XRD spectra of C18-POM LB films. Three different samples with (a) 31, (b) 21, and (c) 11 deposition layers were respectively examined.

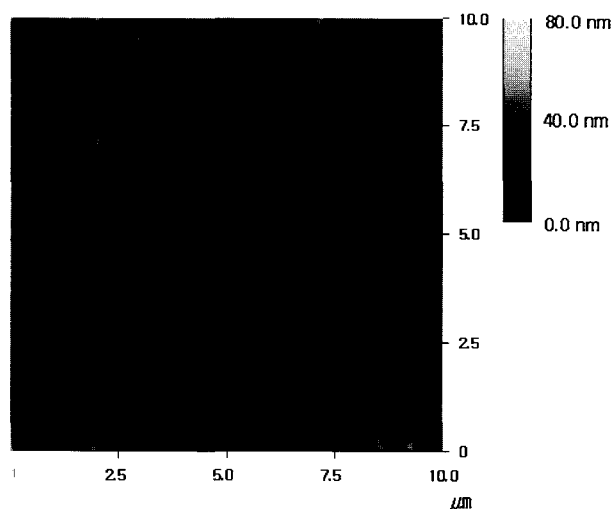


Fig. 5 AFM image of C18-POM LB film scanned by tapping mode.

4. Conclusion

Although the spreading of C18-POM was not carried out to be a complete monolayer, very stable C18-POM layers were formed on water subphase. Specifically, we could demonstrate the orientation control of nanoparticles by introducing a functional group on one side of the surfaces and employing the LB technique. That is, the carboxyl side of the POM is always positioned toward air at the water surface because of the ester hydrophobic long chain. Therefore, when the nanoparticle contains functional elements such as a magnetic atom with unpaired spin and luminescent atomic group, this control of nanoparticle orientation is expected to show efficient functionality in the LE films.

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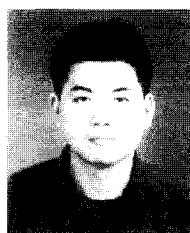
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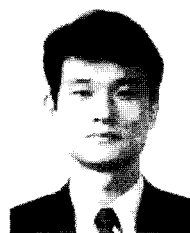
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