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Two-Dimensional Array of Polyoxomolybdate Nanoball Constructed by Langmuir−Blodgett Semiamphiphilic Method

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A two-dimensional array of polyoxomolybdate nanoball ($[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]^{42-}$, Mo_{132}) was successfully constructed by a Langmuir−Blodgett (LB) semiamphiphilic method by using Mo_{132} aqueous solution as a subphase and dimethyldioctadecylammonium (DODA) as a cationic amphiphile. Conservation of molecular structure of the Mo_{132} nanoball in the built-up LB film was confirmed by ultraviolet−visible (UV−vis) and infrared (IR) spectroscopy. Specular X-ray reflectivity (SXR) measurements combined with UV−vis spectroscopy revealed that the Mo_{132}/DODA LB film had a well-defined layered structure containing a densely packed two-dimensional array of the Mo_{132} nanoballs. The electrochemical characteristics of the Mo_{132} nanoballs were retained after the deposition onto the solid substrates, which verifies that the LB semiamphiphilic method is an effective way to fabricate thin films composed of functional nanosized clusters toward a two-dimensional molecular device.

Introduction

Layered materials are formed by stacking two-dimensional compounds or molecules and have a distinct anisotropy in their structures. This structural anisotropy often results in the emergence of interesting properties such as electronic conductivity, semiconductivity, or intercalation.[1−3] One possible method to construct layered materials is the conventional Langmuir−Blodgett (LB) technique, which provides homogeneous thin films with well-defined layered structure.[4] The thickness of the built-up LB films is precisely tunable in a molecular level, and a wide variety of components can be selected. Various stable inorganic components are promising candidates for the construction of functional LB films.

Polyoxometalates (POMs) have great potential as components of this type of films because of their variety of physicochemical properties.[5] Several LB films containing magnetic, electrochemical, and luminescent POM molecules have been fabricated.[6−14] An effective way for the construction of the POM LB films is the "semiamphiphilic method".[6,7] This uses POM aqueous solution as a subphase instead of pure water, on which cationic amphiphiles are spread to form a stable Langmuir monolayer at the air−solution interface.

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The LB film fabricated by this method is composed of densely packed POM monolayers and amphiphile bilayers, and even two-dimensional periodic arrays of POM molecules can be constructed in the built-up LB films.[14]

Recently, large POM molecules (>2 nm in size) with high nuclearity have been synthesized,[15−18] and their related materials have been characterized.[19,20] These POMs with the size comparable to small proteins are quite interesting as components for the LB film fabrication. Pioneering works for thin films containing the high nuclearity POMs have been reported: layer-by-layer films consisting of naked POM,[21] and LB films of surfactant-encapsulated POM (SE-POM).[11,12] In the case of the layer-by-layer films, the surface coverage of POMs was around 50%. On the other hand, the LB films of SE-POM were formed by densely packed layers of SE-POM, in which the packing of POM anions was not a compact one due to the presence of surfactant shell around the individual POM anions.

Here, we successfully constructed a densely packed two-dimensional array of polyoxomolybdate nanoball, ($[\mathrm{Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}}]^{42-}$, $\mathrm{Mo_{132}}$, inside Figure 1), by the LB semiamphiphilic method. The $\mathrm{Mo_{132}}$ nanoball having acetate ligands was prepared by Müller's method,[15b] and dimethyldioctadecylammonium (DODA) was used as cationic partner. The internal layered structure of the $\mathrm{Mo_{132}}$/DODA LB film was investigated by specular X-ray reflectivity (SXR) measurements. The conservation of molecular structure as well as electrochemical characteristics was confirmed.

Experimental Section

Reagents and Materials. Polyoxomolybdate nanoball, $[\mathrm{Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}}]^{42-}$ ($\mathrm{Mo_{132}}$), was prepared as ammonium salt by the literature method.[15b] Dimethyldioctadecylammonium bromide (DODA·Br, Kanto), *N,N′*-di-*n*-octadecylmethylamine (DODMA, Tokyo Chemical Industry), behenic acid ($\mathrm{CH_3(CH_2)_{20}COOH}$, BA, Aldrich), and chloroform (Kanto) were used without further purification. Subphese solutions were prepared with ultrapure water (~18 MΩ cm) delivered from a TORAYPURE LV-08 (TORAY) system. ZnSe sustrates (Ohyo Koken Kogyo Co., Ltd.) and ITO electrodes (I-type 10 Ω/sq, Matsuzaki-Shinku Co.) were cleaned by sequential sonication in dichloromethane, acetone, and distilled water prior to each experiment.

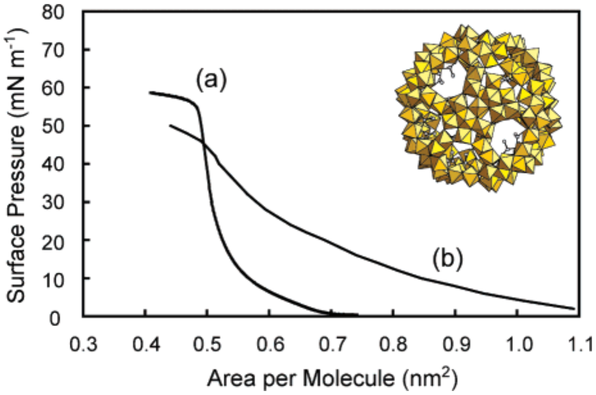

Figure 1. Surface pressure−area (π−A) isotherms of DODA·Br on (a) $\mathrm{Mo_{132}}$ aqueous solution (6×10^{-7} M) and (b) pure water. Polyhedral representation of polyoxometalate nanoball ($\mathrm{Mo_{132}}$) structure is also demonstrated.

LB Film Fabrication. LB films were fabricated by spreading a chloroform solution of DODA·Br (1 mM) onto $\mathrm{Mo_{132}}$ aqueous solutions (6×10^{-7} M) on a KSV3000 apparatus (KSV Instruments). The compression procedure was carried out with a rate of 15 or 30 cm^2 min^{-1} at a subphase temperature of 20 ± 1 °C. After the solvent was evaporated, the floating layer was compressed up to 30 mN m^{-1}, and a stable Langmuir monolayer of DODA·Br was subsequently deposited onto ZnSe (for infrared spectroscopy), ITO (for cyclic voltammetry), or hydrophobic quartz substrates (for other measurements) by the vertical dipping method with a rate of 10 mm min^{-1} under a $\mathrm{N_2}$-purged atmosphere. The hydrophobic quartz substrates used here were prepared by the deposition of three Langmuir monolayers of DODMA or BA onto naked quartz substrates. The number of monolayers of LB film is equal to the number of immersion and emersion processes, on each of which a floating Langmuir monolayer was transferred onto the substrate.

Instrumentation and Methods. Ultraviolet−visible (UV−vis) and infrared (IR) spectra were measured on a JASCO V-570 spectrometer and a JASCO FT/IR-40 spectrometer, respectively. Specular X-ray reflectivity (SXR) measurements were performed on a RINT-TTR diffractometer (rotor X-ray source, Cu Kα 0.154 nm, 60 kV/300 mA) with a parabolic multilayered mirror (at Rigaku Corporation). Rigaku *GXRR* software was used for curve-fitting of SXR profiles by using experimental data from $2\theta = 0.3$ through 6°. A JEOL JSPM-4210 was employed for atomic force microscopy (AFM) measurements in air at ambient temperature. Noncontact mode imaging used silicon cantilevers with a spring constant of 4.5 N/m. Cyclic voltammetric measurements were performed on an Autolab PGSTAT12 potentiostat/galvanostat for the $\mathrm{Mo_{132}}$/DODA LB films deposited onto ITO glass slides (ca. 1 × 4 cm) as working electrodes, while on a SEIKO EG&G model 394 equipped with a static mercury drop electrode for $\mathrm{Mo_{132}}$ aqueous solutions. A Ag/AgCl (saturated KCl) reference electrode and a Pt-wire counter electrode were used for the measurements. The electrolyte was $\mathrm{H_2O}$ (Millipore Q-grade, 18.2 MΩ cm) containing $\mathrm{NaHSO_4}$ (10 mM for the $\mathrm{Mo_{132}}$/DODA LB films and 1 mM for the $\mathrm{Mo_{132}}$ aqueous solutions).

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Results and Discussion

Surface Pressure−Area Isotherms. Figure 1 shows surface pressure−area ($\pi-A$) isotherms of DODA·Br on a Mo$_{132}$ aqueous solution (6×10^{-7} M) and pure water. The isotherm on the Mo$_{132}$ aqueous solution (Figure 1a) exhibited a decrease in the molecular area and was steeper at the end of the compression compared with the case of pure water (Figure 1b), indicating the formation of a dense layer of DODA·Br molecules at the air−solution interface. The anion charge of Mo$_{132}$ is considered to decrease the repulsion between DODA cations.[6,7,22] The hypothetical molecular area of DODA on the Mo$_{132}$ solution was estimated to be 0.53 nm^2 by extrapolating the isotherm in the condensed region to zero pressure. This value was close to the cross-section of hydrophilic head of DODA (0.57 nm^2),[23] suggesting the close packing of DODA on the Mo$_{132}$ solution. After the surface pressure was kept at 30 mN m^{-1}, a stable Langmuir monolayer was formed.

LB Film Fabrication. Mo$_{132}$/DODA LB multilayer films were successfully deposited by the vertical lifting method onto hydrophobic substrates such as ZnSe and quartz with three monolayers of DODMA or BA, whereas only the Mo$_{132}$/DODA LB monolayer was fabricated onto a hydrophilic substrates (see below). The transfer ratio was almost unity for both the immersion (↓) and emersion (↑) processes, indicating the formation of Y-type LB films. The Mo$_{132}$/DODA LB films deposited on quartz substrates exhibited a strong brown color even after the deposition of a few monolayers.

Figure 2a shows UV−vis spectra of Mo$_{132}$/DODA LB film deposited on a hydrophobic quartz (30 monolayers) and Mo$_{132}$ aqueous solution. Both spectra exhibited intense O → Mo ligand-to-metal charge-transfer (LMCT) absorption in the region below 300 nm as well as a broad peak in the visible region (~450 nm), demonstrating that the Mo$_{132}$ nanoballs were successfully organized onto the quartz substrate. The broad peak in the visible region was observed at 488 nm for the Mo$_{132}$/DODA LB film, and red-shifted from 453 nm for the Mo$_{132}$ aqueous solution, which may be due to two-dimensional organization into the built-up LB films.

The ratio of DODA to Mo$_{132}$ in the LB film was estimated from the results above. The number of DODA molecules in the LB film is easily evaluated from the size of the substrate, the transfer ratio and the molecular area at the deposition surface pressure. On the other hand, the quantity of Mo$_{132}$ deposited onto the LB film can be calculated from the absorbance in the UV−vis spectra of the DODA/Mo$_{132}$ LB films by using the value of molar absorption coefficient of the Mo$_{132}$ aqueous solution ($\epsilon = 2.9 \times 10^5$ cm^2 mmol^{-1} (M^{-1} cm^{-1}) at 453 nm). The quantity of DODA and Mo$_{132}$ in the LB film was estimated to be 1.2×10^{-7} mol and $(3.0 \pm 0.3) \times 10^{-9}$ mol, respectively. This corresponds to a DODA:Mo$_{132}$ ratio of (40 ± 4):1, comparable to the value of the negative charge (−42) of Mo$_{132}$. Therefore, the cation exchange of the Mo$_{132}$ into DODA almost completely proceeded at the air−solution interface when the stable Langmuir monolayer of DODA formed, which was also confirmed by IR spectra (see below).

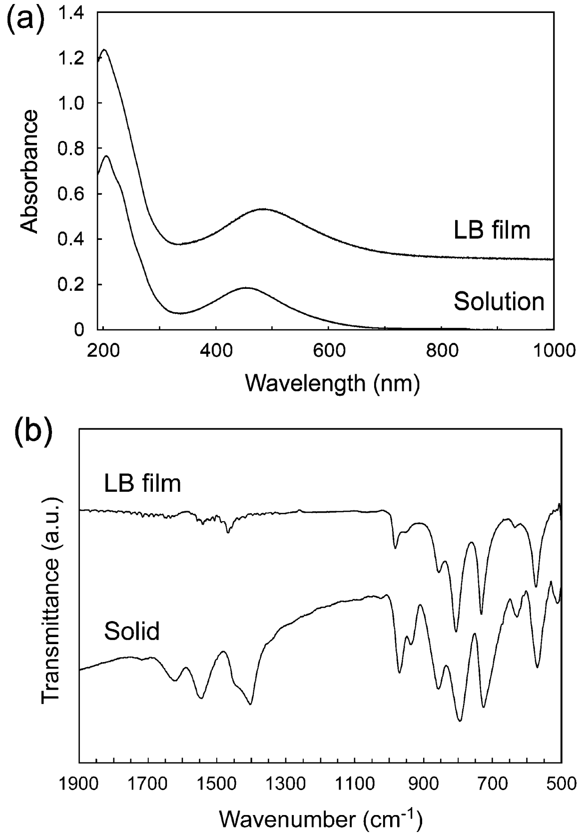

Figure 2. (a) UV−vis spectra of Mo$_{132}$/DODA LB film (30 monolayers deposited on a hydrophobic quartz substrate with three monolayers of DODMA) and Mo$_{132}$ aqueous solution (6.3×10^{-7} M). (b) IR spectra of Mo$_{132}$/DODA LB film (28 monolayers deposited on a ZnSe substrate) and Mo$_{132}$ solid (KBr pellet).

IR spectroscopy confirmed the conservation of molecular structure of Mo$_{132}$ after the organization onto the solid substrates. Figure 2b demonstrates IR spectra of the Mo$_{132}$/DODA LB film and Mo$_{132}$ solid, which exhibited characteristic peaks for Mo$_{132}$ in the region below 1000 cm^{-1}. The peaks in the spectrum for the Mo$_{132}$/DODA LB film (983, 952, 855, 806, 733, 634, 574 cm^{-1}) slightly shifted to a higher region from the corresponding peaks of the Mo$_{132}$ solid (970, 936, 857, 795, 726, 629, 570 cm^{-1}). This is considered to be due to two-dimensional organization and lower hydration of the Mo$_{132}$ anions in the LB films.[6] On the other hand, because the band at 1403 cm^{-1} of the NH$_4^+$ counter cations disappeared in the IR spectra of the LB film, we can conclude that DODA molecules substituted NH$_4^+$ during the LB film formation.

Internal Structure of LB Film. SXR measurements revealed a well-defined layered structure in the Mo$_{132}$/DODA LB film. Figure 3a demonstrates an experimental SXR profile for Mo$_{132}$/DODA LB film with 30 monolayers, which exhibited distinct Bragg peaks as well as Kiessig fringes. These Bragg peaks can be assigned to 001 and 002 reflections, demonstrating a well-defined layered structure

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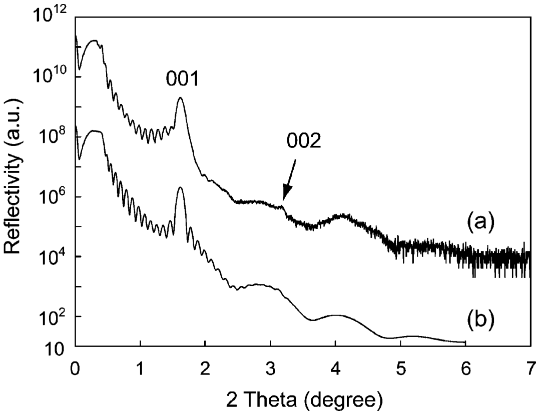

Figure 3. SXR profiles of Mo_{132}/DODA LB film with 28 monolayers deposited on a quartz substrate with three monolayers of BA: (a) experimental and (b) fitted profile. Experimental data in the range of $2\theta = 0.3-6°$ were used for the fitting. Indices for Bragg reflections are in the figure.

consisting of stacks of Mo_{132} and DODA layers along the growth direction. The periodicity of the layered structure calculated from the Bragg peak positions was 5.6 nm, which was confirmed by the fitting procedure (see below). This value of periodicity was much higher than that obtained for the surfactant-encapsulated-Mo_{132} LB films reported in the literature that had a value of 4.2 nm,[12] indicating that the two methods give rise to a very different organization of the Mo_{132} nanoballs within the LB film. The higher periodicity of the LB films prepared by the semiamphiphilic method may be indicative of a more dense packing of the Mo_{132} nanoballs. This was confirmed by SXR profile fitting and the estimation of the area occupied by individual Mo_{132} in the inorganic monolayer (see below).

The composition of the layered structure in the Mo_{132}/DODA LB film was elucidated by the SXR profile fitting. The fitting procedure can provide optimized values of the density, layer thickness, and surface roughness for each layer on the basis of X-ray reflection theory.[24] DODA cations are considered to form a bilayer arrangement between the inorganic Mo_{132} monolayers in the LB film as other POM LB films[6−10,14] or related POM crystals,[25] and an ideal structure model can be assumed as shown in Figure 4a. A successful fit (Figure 3b) for the SXR profiles reproduced the essential feature of the experimental SXR profile (Figure 3a), indicating the validity of the ideal layered structure depicted in Figure 4a. Namely, the Mo_{132}/DODA LB film with 28 monolayers (Figure 3a) consisted of 28 monolayers of DODA and 14 (28/2) monolayers of Mo_{132}. Broad fringelike structures observed in $2\theta = 2.5-6°$ seem due to the BA layers predeposited onto the quartz substrate. The successful fitting described above clearly demonstrates that well-defined monolayers of Mo_{132} were constructed in the LB film and that the LB semiamphiphilic method employed here effectively produced a two-dimensional molecular array as the monolayer of Mo_{132}, even in the case of large nanosized molecules.

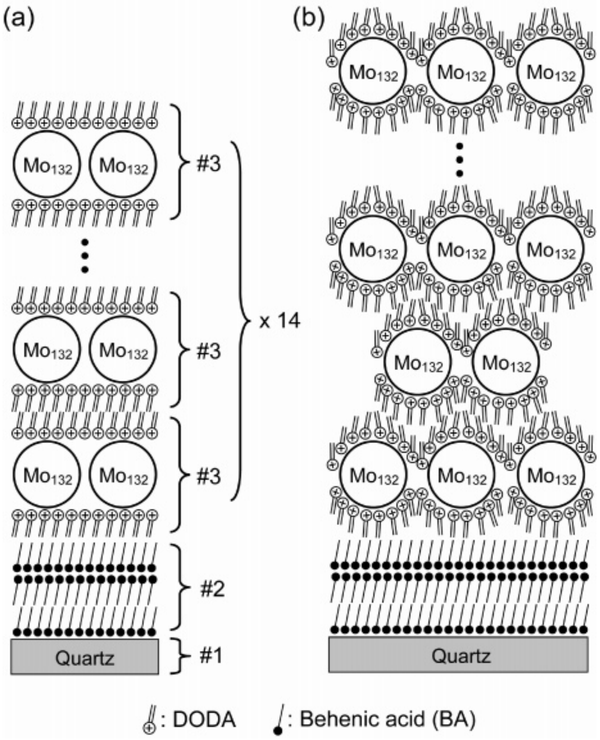

Figure 4. Structure models of Mo_{132}/DODA LB film: (a) ideal model used for SXR profile fitting, and (b) plausible model of internal structure.

Table 1. Fitting Parameters for the SXR Profile of Mo_{132}/DODA LB Film (28 Monolayers) Deposited on a Hydrophobic Quartz Substrate with Three Monolayers of Behenic Acid (BA)[a]

stack number	repeat of stack	layer consisting of stack	density (g cm^{-3})	thickness (nm)	roughness (nm)
3	14	DODA (monolayer)	0.53	1.31	1.80
		Mo_{132} (monolayer)	3.56	2.65	1.66
		DODA (monolayer)	1.14	1.69	1.48
2	1	BA (three monolayers)	2.38	7.40	0.51
1	−	quartz (substrate)	2.21	−	0.50

[a] Experimental data in the range of $2\theta = 0.26-6°$ were used. Fitting procedure was performed with Rigaku *GXRR* software.

The internal thicknesses of the Mo_{132} monolayer and DODA monolayers (above and beneath the Mo_{132} monolayer) were 2.65, 1.31, and 1.69 nm, respectively (Table 1). The summation of these fitted values (5.65 nm) represents the periodicity of the layered structure in the Mo_{132}/DODA LB film, which coincided with the value calculated from the Bragg peak positions (5.6 nm, mentioned above). The thickness of the Mo_{132} monolayer (2.65 nm) was slightly thinner than the diameter of the Mo_{132} nanoball (∼3 nm).[15,16b] On the other hand, the thicknesses of the DODA monolayers were smaller than the conceivable thickness (∼2 nm) anticipated from the length of DODA aliphatic chain (ca. 2.3 nm).[26] This is probably due to the relatively large roughness (1.5−1.8 nm, Table 1) of each monolayer caused by the large size of Mo_{132}. A more plausible structure model is demonstrated in Figure 4b, where DODA cations would have a much more disordered arrangement than the ideal

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(26) Average length of bended and non-bended octadecyl chains of DODA estimated from $(DODA)_2Mo_6O_{19}$ crystal structure[25a] by using *Diamond 3* (Crystal Impact).

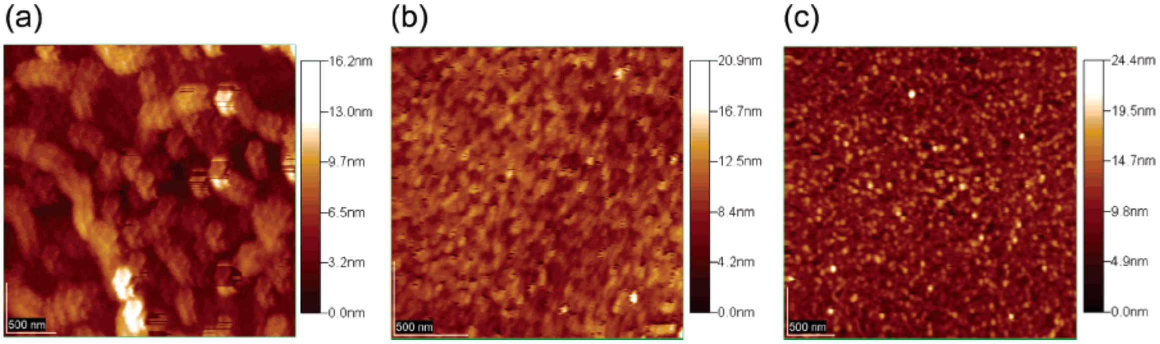

Figure 5. AFM images of Mo$_{132}$/DODA LB films: (a) one monolayer deposited on a naked quartz substrate, (b) six monolayers deposited on a hydrophobic quartz substrate with three monolayers of BA, and (c) 10 monolayers deposited on a hydrophobic quartz substrate with three monolayers of BA.

layered structure (Figure 4a). DODA cations would deeply enter into the cavity between the Mo$_{132}$ anions to form a rougher and more fused interface between each monolayer, which would result in a more disordered layered structure.

The area occupied by individual Mo$_{132}$ in the two-dimensional molecular array was estimated from the UV−vis spectra (Figure 2a). The surface concentration, Γ, of each Mo$_{132}$ monolayer can be calculated by the equation of $\Gamma = [N_A A/(l\epsilon)]$, where N_A is Avogadro's number, A is the absorbance of the broad peak in the visible region, l is the total number of the Mo$_{132}$ monolayers, and ϵ is the molar absorption coefficient (2.9×10^5 cm^2 mmol^{-1}, the value for the aqueous solution).[21] The LB film measured in Figure 2a (with 30 monolayers) had 15 (30/2) monolayers of Mo$_{132}$ in each side of the substrate, meaning that 30 monolayers of Mo$_{132}$ were deposited onto the LB film in total. Thus, the Γ for Mo$_{132}$ was estimated to be 6.9 ± 0.6 nm^2 cluster^{-1}, meaning the area occupied by individual Mo$_{132}$. Although this value was smaller than the molecular cross section of Mo$_{132}$ (8.5 nm^2),[27] it is believed that the two-dimensional array of Mo$_{132}$ in the LB film had a close and dense packing when the film fabricated by the LB semiamphiphilic method. The smaller value may be due to the slight distortion of the Mo$_{132}$ framework sandwiched by DODA layers and change of electronic property, which may increase the molar absorption coefficient of the Mo$_{132}$ nanoball in the LB film. This value of the area occupied by individual Mo$_{132}$ (6.9 ± 0.6 nm^2 cluster^{-1}) was much smaller value than that of other thin films composed of Mo$_{132}$ described in the literature prepared by the layer-by-layer self-assembly method (22.7 ± 1.0 nm^2 cluster^{-1}),[21a] demonstrating that the LB semiamphiphilic method is quite effective in order to construct densely packed two-dimensional molecular arrays of the Mo$_{132}$ nanoball on solid substrates.

Surface Structure of LB film. General surface structures of the Mo$_{132}$/DODA LB films were investigated by noncontact AFM. Figure 5a shows an AFM image of the Mo$_{132}$/DODA LB films with one monolayer deposited on a naked hydrophilic quartz substrate. The surface had heterogeneous domain structures with a height of 5.8 nm. The height of the domains was similar to the periodicity of the layered structure in the Mo$_{132}$/DODA LB films revealed by the SXR measurements.

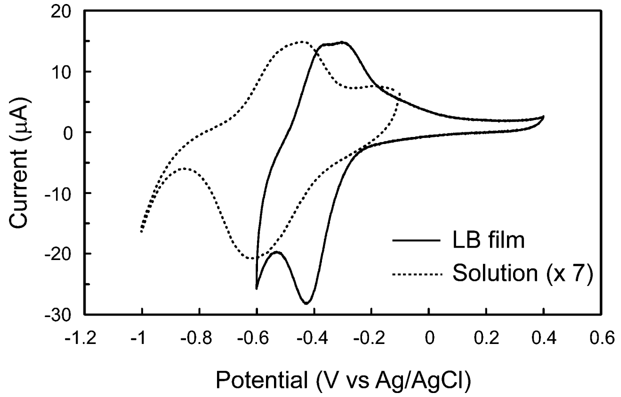

Figure 6. Cyclic voltammograms of Mo$_{132}$/DODA LB film (three monolayers deposited on an ITO substrate, solid line, in 100 mM NaHSO$_4$) and Mo$_{132}$ aqueous solution (dotted line, hanging mercury electrode, 2 μM in 1 mM NaHSO$_4$). Sweep rate = 100 mV s^{-1}.

On the contrary, the Mo$_{132}$/DODA LB films with 6 and 10 monolayers deposited onto the hydrophobic substrates generally had homogeneous surfaces (images b and c of Figure 5). Particulate structures with a size of 50−80 nm were observed for each LB film. The Mo$_{132}$/DODA LB film with 10 monolayers (Figure 5c) had particulate structures of smaller diameter than that with 6 monolayers (Figure 5b). In the LB film of six monolayers, the difference of height between the lowest and highest zones lay around the height of one monolayer (5 nm) with some holes in which this difference was higher (∼10 nm). In the LB film of 10 monolayers the height difference was slightly higher in all the surface (10−15 nm). The high roughness of these LB films which was increased with the number of monolayers would be caused by the large size of Mo$_{132}$ (∼3 nm, Figure 4b) compared with DODA (∼2 nm) rather than the inhomogeneity of the LB film structure.

Electrochemical Characteristics. Electrochemical features of the Mo$_{132}$/DODA LB film with three monolayers deposited onto an ITO electrode were compared with those of the Mo$_{132}$ aqueous solution. Figure 6 demonstrates cyclic voltammograms of the Mo$_{132}$/DODA LB films (solid line) and the solution (dotted line). Both voltammetric profiles exhibited a set of quasi-reversible peaks: a cathodic peak at −0.43 V and anodic peak at −0.30 V for the LB films, with a cathodic peak at −0.62 V and anodic peak at −0.44 V for the solution. The Mo$_{132}$/DODA LB film exhibited the similar voltammetric behavior to that for the aqueous solution, indicating that the electrochemical characteristics of Mo$_{132}$ were retained after the organization onto the solid substrate.

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(27) Estimated value from space-filling model of the Mo$_{132}$ crystal structure[16b] by using *Diamond 3* (Crystal Impact).

The separation between cathodic and anodic peak potential for the LB film (0.13 V) was comparable to that for the aqueous solution (0.18 V). The anodic and cathodic peak potentials for the LB film positively shifted with respect to the solution. This may be a charge effect arising from two-dimensional incorporation of positively charged DODA molecules within the LB film with respect to solution.

Conclusions

The LB semiamphiphilic method enabled us to construct the LB film of the Mo_{132} nanoball having a well-defined layered structure. SXR measurements combined with UV–vis spectroscopy revealed the formation of a densely packed two-dimensional array of Mo_{132} in the LB film, which is the most densely packed Mo_{132} nanoball deposited onto the solid substrate to date. The molecular structure and electrochemical characteristics of Mo_{132} were retained after the deposition. The results presented here verify the effectiveness of the LB semiamphiphilic method to construct a densely packed two-dimensional array consisting of not only conventional POM but also nanosized high-nuclearity POM. Such a two-dimensional POM array could be employed for the construction of POM-based molecular devices on the solid substrates.

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