Highly Conductive Inorganic−Organic Hybrid Langmuir−Blodgett Films Based on MoS_2

Hiroaki Tachibana,*,† Yasushi Yamanaka,‡ Hideki Sakai,‡ Masahiko Abe,‡ and Mutsuyoshi Matsumoto†

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305-8565, Japan and Science University of Tokyo, 2641 Yamazaki, Noda 278-8510, Japan

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Highly conductive hybrid Langmuir−Blodgett (LB) films of MoS_2 and amphiphilic compounds such as alkylammonium halides and alkylamines were fabricated. The interlayer spacing of the LB films depended on the organic species. The lateral conductivity of 10-layer LB films was in the range of 10^1 to 10^2 S cm^{-1} and decreased with an increase in interlayer spacing. The conductivity of 10^2 S cm^{-1} is the highest value for LB films reported so far. The conductivity of the LB films increased with the layer number and became constant when the layer number was sufficiently large. The conductivity was stable at room temperature even for single-layer LB films and decreased by less than an order of magnitude during four months.

Introduction

Inorganic−organic hybrid molecular materials have been attracting considerable attention because they provide materials with novel structures and functions.[1,2] The exfoliation of layered materials followed by the Langmuir−Blodgett (LB) technique,[3−5] the layer-by-layer self-assembling method,[6,7] and spin coating[8] has been used to fabricate inorganic−organic alternate-layered hybrid ultrathin films. Inorganic species such as transition metal dichalcogenide,[3,4,6] clays,[5] α-zirconium phosphate,[7] and titanate[8] have been used as the layered materials. In particular, MoS_2 was exfoliated by intercalation with Li, followed by the reaction with water. By spreading long-chain ammonium halides on the dispersion of single-layer platelets of MoS_2, inorganic−organic hybrid monolayers were obtained, which were transferred onto solid substrates using the LB technique.[3] Further, we have demonstrated that it is possible to extend this method to fabricate hybrid LB films based on other transition metal dichalcogenides such as $MoSe_2$ and WS_2.[4] The hybrid LB films showed high conductivity at room temperature. Among them, the hybrid LB films based on MoS_2 exhibited the highest conductivity of more than 10 S cm^{-1}.

In this paper, we report the effect of the organic species and the layer number on the conductivity of the hybrid LB films based on MoS_2. We have revealed that the interlayer electronic coupling between the inorganic layers contribute significantly to the lateral conductivity of the LB films. Furthermore, we have found that the conductivity is the highest for LB films and very stable in air at room temperature.

Experimental Section

Materials. MoS_2 powder (99.9%) was purchased from High Purity Chemicals Laboratory. The 1.6 M hexane solution of *n*-butyllithium (Wako Chemical Co.) and 1,1,1,3,3,3-hexamethyldisilazane (Nacalai Tesque) were used as received. Primary, secondary, and tertiary long-chain alkylammonium halides and alkylamines were available from Toyo Gosei Kogyo Co. and Tokyo Kasei Kogyo Co. Alkylammonium halides and alkylamines were abbreviated as *m*C*n*-N and *m*C*n*-A, respectively, where *m* and *n* are the number and the length of alkyl chains, respectively ($1 \leq m \leq 3$, $10 \leq n \leq 22$). Molecules of *m*C*n*-A possess $(4 - m)$ methyl groups attached to the nitrogen. Chloroform of spectroscopic grade (Dojindo Laboratories) was used as a spreading solvent.

Exfoliation of MoS_2. The suspension of MoS_2 single layers were prepared following the procedure reported previously.[9] MoS_2 powder was stirred in 1.6 M hexane solution of *n*-butyllithium for 48 h under nitrogen at room temperature. The solid was collected by filtration and then washed with hexane under nitrogen. The obtained solid was cast into pure water and was stirred under ultrasonication for 30 min to give suspension of single-layer particles of MoS_2. To remove LiOH, the suspension was dialyzed until the pH of the washing water was less than 7. The concentration of the suspension was adjusted to 0.3 g/L by dilution with pure water.

Preparation of LB Films. LB films were prepared using a Lauda film balance at 17 °C. Chloroform solution of an alkylammonium halide or an alkylamine was spread on the suspension of MoS_2. The monolayers were transferred at 25

† National Institute of Materials and Chemical Research.
‡ Science University of Tokyo.

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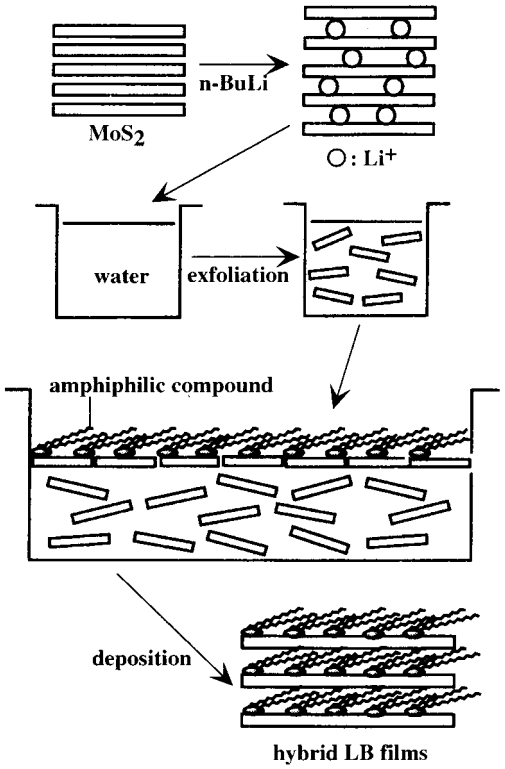

Figure 1. Scheme of the preparation of the hybrid monolayers based on MoS_2 at the air−water interface and structure in the hybrid LB films.

mN m^{-1} onto solid substrates using the horizontal lifting method. For X-ray diffraction (XRD) and XPS measurements, glass plates hydrophobized with 1,1,1,3,3,3-hexamethyldisilazane were used as the solid substrates. For the measurements of the lateral conductivity of the LB films, gold electrodes with a gap distance of 0.4 mm were formed on the glass plates by vacuum deposition before the fabrication of the LB films.

Characterization. XRD patterns were recorded on a Philips PW1800 system equipped with Cu Kα X-ray radiation. Measurements were made in a stepwise manner with a step of 0.1° (θ), at a scan speed of 15 s per step. XPS spectra were obtained on a Perkin-Elmer PHI 5600ci ESCA system with monochromated Al Kα radiation. Measurements were carried out with a resolution of 1.8 and 0.4 eV for the overall and narrow scan, respectively, with a takeoff angle of 45°. Binding energies were calibrated by referring to the aliphatic C 1s line at 284.5 eV. The lateral conductivity of the LB films was measured at room temperature by a dc two-probe method. For the stability measurements, the conductivity of the LB films was monitored while keeping the films at room temperature in the dark.

Results and Discussion

Figure 2 shows typical XRD patterns of the hybrid LB films. For comparison, the XRD pattern of unexfoliated MoS_2 powder is included. A strong diffraction peak is seen in the XRD pattern of the MoS_2 powder. The d(001) value is 6.1 Å, which corresponds to the thickness of a single layer of MoS_2. On the other hand, two features are evident in the XRD patterns of the hybrid LB films. First, only a progression of (00l) peaks are seen. Second, the d(001) value depends on the organic species, and is in the range of 10−20 Å. These results indicate that the LB films have layered hybrid structures of MoS_2 and amphiphilic compounds. The length of the organic species used in this study was

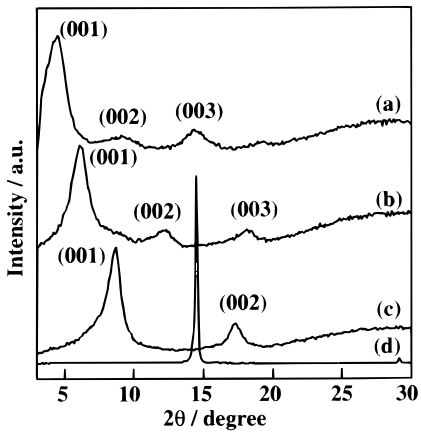

Figure 2. X-ray diffraction patterns of 10-layer hybrid LB films of MoS_2 and amphiphilic compounds: (a) 3C18-N, (b) 3C10-A, and (c) 2C10-A. For comparison, the XRD pattern of unexfoliated MoS_2 powder (d) is included.

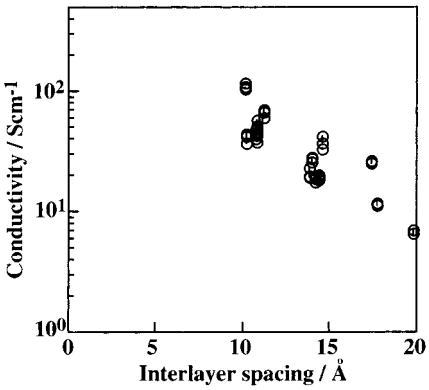

Figure 3. Lateral conductivity of 10-layer LB films at room temperature as a function of interlayer spacing.

estimated to be in the range of 14−29 Å, on the basis of the CPK model. The alkyl chains should be considerably tilted with respect to the surface normal and, in some cases, should be almost parallel to the film surface.

Figure 3 shows the room-temperature conductivity of the hybrid LB films as a function of interlayer spacing of the films. It is evident that the conductivity is very high. The hybrid LB films with an interlayer spacing of 10 Å exhibit the conductivity of 100 S cm^{-1}, which is the highest value for LB films.[10−12] This value is far larger than the value of 3.3×10^{-7} S cm^{-1} for compressed pellet of unexfoliated MoS_2 powder. The hybrid LB films have alternate layered structures in which inorganic layers are sandwiched by organic layers. The inorganic layers consist of MoS_2 single-layer particles, which are closely packed in two dimensions. The conductivity of the LB films should be associated with the MoS_2 layers because the organic layers can be considered as insulating.

To explain the high conductivity of the LB films, we should consider the intrinsic and extrinsic factors affecting the conductivity. The most probable mechanism

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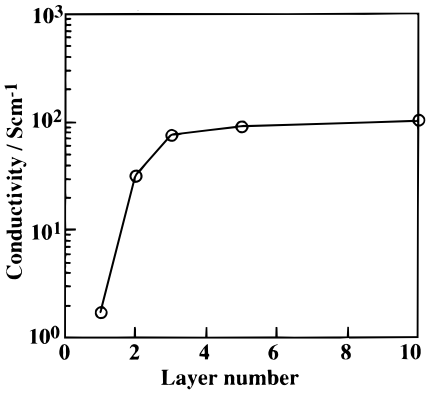

Figure 4. Lateral conductivity as a function of layer number for the hybrid LB films of MoS_2 and 1C18-A.

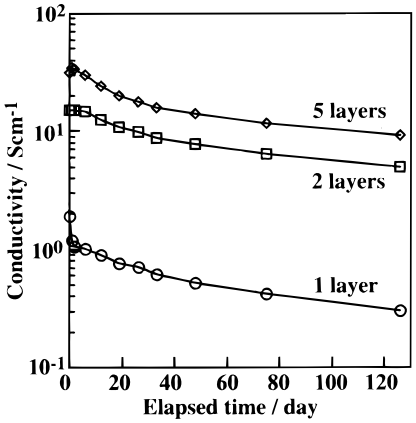

Figure 5. Time course of the lateral conductivity of the hybrid LB films of MoS_2 and 2C18-N with various layer numbers.

of the high conductivity should be the structural transformation from 2H-MoS_2 to metastable 1T-MoS_2 structure accompanied by the change in the electronic band structure of MoS_2, induced by the intercalation−exfoliation process.[13,14] This is supported by the fact that the restacked pellet of MoS_2 powder after the intercalation−exfoliation treatment showed the conductivity of 1.2×10^{-1} S cm^{-1}, which is about 6 orders of magnitude higher than the one of the unexfoliated powder. The possibility that the oxidation state of Mo differs from +4 has been denied by the results of XPS measurements of the LB films. In the XPS spectra of the LB films, only two bands without shoulders were observed for Mo atoms at 228.6 and 231.8 eV, which are assigned to $3d_{5/2}$ and $3d_{3/2}$ bands of Mo, respectively. This indicates that all the Mo atoms are in the Mo^{4+} state in the LB films.[15,16] As an extrinsic factor, we should consider that the MoS_2 single-layer particles are closely packed two-dimensionally in the inorganic layers in the hybrid LB films. However, this has a tradeoff with the hopping of the carriers in the vertical direction.

Another important point evident in Figure 3 is that the conductivity decreases with an increase in the interlayer spacing. This tendency does not depend on the organic species. This suggests that the role of the organic species is mainly to hold the MoS_2 layers apart and that the packing and the electronic state of MoS_2 particles are essentially the same for all the LB films with the same interlayer spacing. The electronic coupling between the adjacent inorganic layers should contribute significantly to the lateral conductivity of the LB films.

Figure 4 shows the lateral conductivity of the LB films at room temperature as a function of layer number. It is evident that the lateral conductivity depends on the layer number. On going from a single-layer LB film to a two-layer LB film, the conductivity increases by almost an order of magnitude. Further increase in the layer number increases the conductivity to a lesser extent. Finally the conductivity becomes constant when the layer number is sufficiently large. The conductivity of a single-layer LB film should be determined both by the in-plane conductivity within a MoS_2 single-layer particle and by the relatively small conductivity due to the domain boundaries present in the LB film. The interlayer electronic coupling within multilayer LB films provides pathways for the charge carriers to flow in the vertical direction, which should contribute to the lateral conductivity.

Figure 5 shows the stability of the conductivity of the hybrid LB films at room temperature. It is clear that the conductivity is very stable, irrespective of the layer number. It should be noted that even the conductivity of a single-layer LB film is very stable and that the conductivity decreases by less than an order of magnitude over four months. Such a stability has not been reported for conductive LB films based on charge-transfer complexes or polymers. The decrease in the conductivity of the hybrid LB films with time is probably due to a gradual structural transformation from the metastable 1T-MoS_2 to 2H-MoS_2 structure.

Conclusions

Highly conductive hybrid ultrathin films containing MoS_2 were prepared by using the intercalation−exfoliation method coupled with the LB technique. To the best of our knowledge, the hybrid films show the highest conductivity for LB films. The conductivity is high and stable even for single-layer LB films. It should be noted that the interlayer electronic coupling between the adjacent inorganic layers contributes significantly to the lateral conductivity. These results indicate that a suitable combination of inorganic and organic species will give novel hybrid materials with higher conductivity.

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