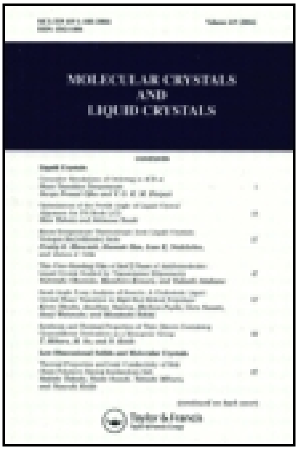

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# Highly Electrical Conductivity of Hybrid Langmuir-Blodgett Films of Transition Metal Dichalcogenide and Amphiphilic Compounds

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Hybrid alternate layered films of transition metal dichalcogenides and amphiphilic compounds were prepared by Langmuir-Blodgett (LB) technique. The conductivity at room temperature depended on the transition metal dichalcogenide species, showing the highest value for the hybrid LB films of $MoS_2$ system. This methodology was successfully applied to the fabrication of the hybrid LB films using various organic amphiphiles such as cyanine dyes, phthalocyanines, azobenzene, and ferrocene derivatives. The conductivity depended on the interlayer spacing: the conductivity decreased with increasing interlayer spacing of the film. The highest electrical conductivity of the hybrid LB films was over 100 $Scm^{-1}$.

*Keywords:* transition metal dichalcogenide; Langmuir-Blodgett films; conductivity; amphiphile

## INTRODUCTION

Langmuir-Blodgett (LB) deposition of monolayers from the air-water interface to solid substrates can provide well-ordered mono- and multilayered systems useful for applications such as switching devices[1,2] and optical memories[3,4]. New organic/inorganic nanocomposites have become increasingly attractive, because these materials can improve specific properties of the parent components, thus extending the number of potential applications of the individual components. Recently, we have reported the formation of hybrid alternate layered Langmuir-Blodgett (LB) films of an amphiphilic ammonium cation and $MoS_2$ using the LB technique[5]. This methodology is simple and convenient for preparing hybrid organic/inorganic films in which organic compounds are sandwiched between layers of the inorganic species. The advantage of this method is that organic molecules, transition metal dichalcogenides, and interlayer distance between the transition metal dichalcogenide layers can be changed easily.

In this paper, we report that it is possible to extend this methodology to the fabrication of hybrid LB films of various organic molecules and transition metal dichalcogenides. The electrical conductivity of the hybrid LB films is also examined.

## EXPERIMENTAL

Hybrid LB films of amphiphilic compounds and transition metal dichalcogenide were prepared as shown in Fig. 1. Single molecular layers of $MoS_2$ dispersed in water were prepared by first intercalating lithium using n-butyllithium (n-BuLi) in hexane, then exposing the intercalated compound to excess water, and finally dialyzing the suspension. The dialysis was continued till the washing water became neutral. The concentration of transition metal dichalcogenide of subphase is adjusted by adding pure water into the suspension of transition metal dichalcogenide.

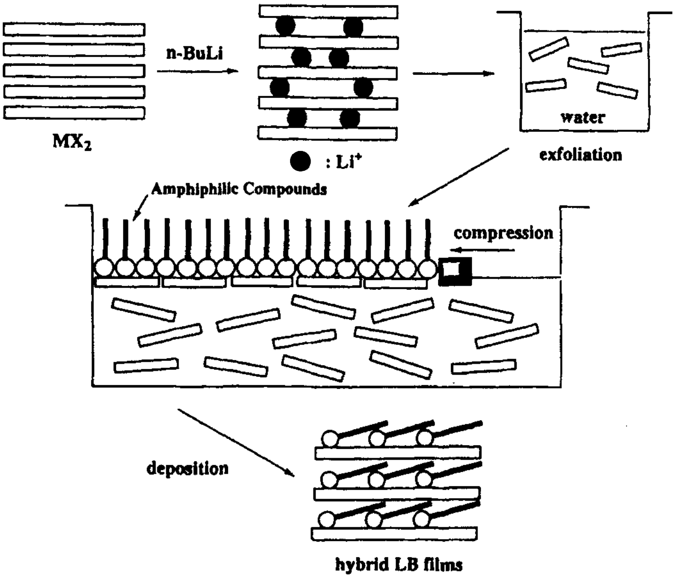

FIGURE 1 Fabrication of hybrid LB films of transition metal dichalcogenide and amphiphilic compound.

The LB technique was performed using a Lauda film balance. Chloroform solution of an amphiphilic compound was spread onto suspension of single layers of transition metal dichalcogenide. The hybrid monolayer was transferred using the horizontal lifting method at 25 $mNm^{-1}$ onto solid substrates. For conductivity measurements, gold electrodes (gap distance, 0.6 mm) were formed on the substrates by vacuum deposition before the transfer of monolayers. The conductivity of the hybrid LB films was measured by a d.c. two-probe method. The interlayer spacing of the hybrid LB films were measured by X-ray diffraction (XRD).

## RESULTS AND DISCUSSIONS

### Effect of Transition Metal Dichalcogenide Species

$MoX_2$ and $WX_2$ having group 6B elements reacted with n-BuLi at room temperature and 100 ℃, respectively, and were intercalated with Li, resulting in a stable suspension of single layers in water. The exfoliation of transition metal dichalcogenides having group 4B elements ($TiS_2$, $ZrS_2$) and 5B elements ($NbS_2$, $NbSe_2$, $TaS_2$) was not successful even at elevated temperatures. In the former case, the exfoliated single layers restacked during dialysis. In contrast, the latter materials were not effectively intercalated with Li.

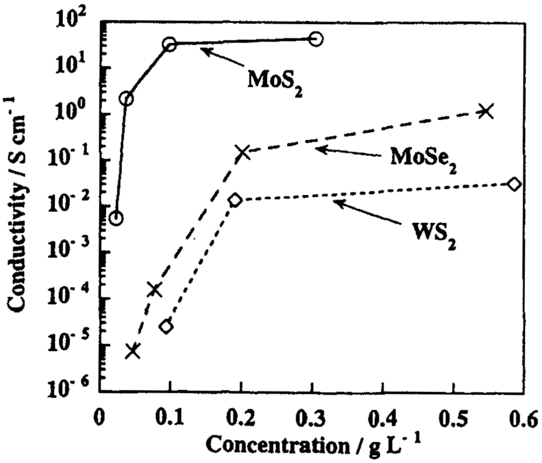

FIGURE 2 Concentration dependence of conductivity in the hybrid LB films of three transition metal dichalcogenide, $MoS_2$, $MoSe_2$, and $WS_2$ with di-n-octadecylammonium cation.

The electrical conductivity of the hybrid LB films at room temperature depended on the transition metal dichalcogenide. Among $MoS_2$, $MoSe_2$, and $WS_2$ which were successfully exfoliated, the conductivity of the hybrid LB films of di-n-octadecylammonium-$MoS_2$ system was 1000 times higher than that of the $WS_2$ system. This difference is probably due to the difference in the band gap and the band structure.

The conductivity was very sensitive to the concentration of each transition metal dichalcogenide dispersed in the subphase. The concentration dependence of the conductivity at room temperature is shown in Fig. 2. The tendency is qualitatively the same for the three hybrid LB films. With increasing the concentration, the conductivity increases rapidly, becomes 1000 times higher than that of the lowest concentration, and then levels off at a certain concentration. The reason of the large conductivity change is not clear at the moment. Considering that virtually the same amount of $MoS_2$ is incorporated in each monolayer irrespective of the $MoS_2$ concentration in the subphase[5], the conductivity may depend strongly on the difference in the mode of accumulation of the $MoS_2$ domains in the films.

### Variation of Organic Component of Hybrid LB Films

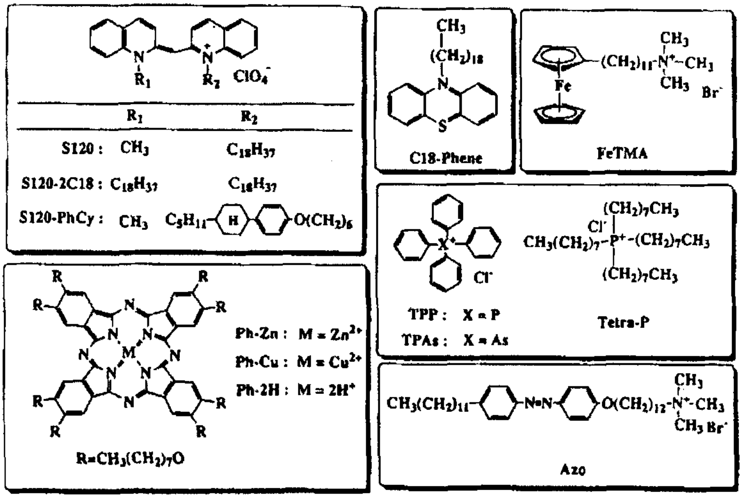

FIGURE 3 Organic compounds used in this study.

We investigated the formation of the layered LB films using various organic molecules having π-electrons as shown in Fig. 3. $MoS_2$ was chosen as the transition metal dichalcogenide because the highest conductivity was obtained as described above. The electrical conductivity of the hybrid LB films is plotted against the interlayer spacing in Fig. 4. All the hybrid LB films were fabricated by transferring monolayers on $MoS_2$ dispersion at the same concentration ( 0.1 $gL^{-1}$).

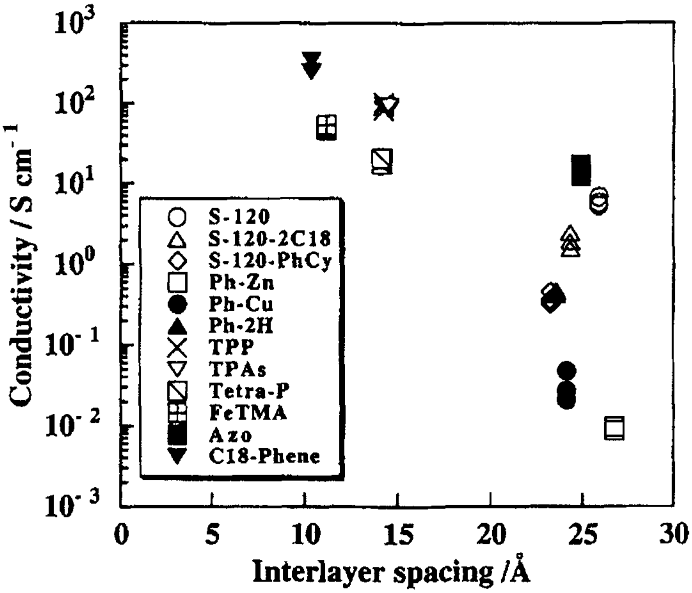

FIGURE 4 Relationship between interlayer spacing and conductivity of the hybrid LB films.

The hybrid LB films showed three features. First, all the organic molecules investigated in this study were incorporated in the hybrid LB films. Second, the interlayer spacing between the $MoS_2$ layers estimated from the analysis of XRD measurements depended on the organic species, probably due to the difference in density, orientation, and bulkiness of the organic molecules. Finally, the electrical conductivity at room temperature of the hybrid LB film depended on the intercalated organic species. This difference in the conductivity arises probably from two factors. One is the interlayer spacing between the $MoS_2$

layers and the other is the electronic properties of the molecules. There is a good correlation between the interlayer spacing and the conductivity. The decreasing conductivity with increasing interlayer spacing suggests that the hopping of the carriers in the direction normal to the film surface plays a significant role in the electrical properties of the films. At around an interlayer spacing of 25 Å, the conductivity of the films ranges over a few orders of magnitude, which may be due to the difference in electronic properties of the intercalated organic species.

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