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Preparation and Structure of Q-State Lead Sulfide Monolayers in Metastable Stearic Acid Langmuir-Blodgett Films

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Monolayers of Q-state PbS were prepared by exposure of Langmuir-Blodgett (LB) films of lead stearate to H_2S at a pressure of 1 Torr. Its long spacing measured by X-ray diffraction is 50.5 ± 0.2 Å which is just the same with that of lead stearate LB films. It was determined by X-ray diffraction and IR that the hydrocarbon chains are still packed in an orthorhombic unit cell after the reaction. The carboxylic groups yielded by the reaction form a ring structure by hydrogen bonds which controls PbS within a monolayer. A structured UV-visible absorption spectrum of the PbS monolayer was obtained. The PbS monolayer consists of a two-dimensional domain or linear form of PbS. The latter is more possible. Their size is almost homogeneous. The onset of the absorption of PbS monolayer is blue-shifted by 1.4 eV with respect to bulk PbS.

Introduction

Barraud's group first recognized that inorganic compounds can be inserted into the polar planes of LB films by chemical reactions.[1] The preparation and properties of Ag small clusters and HgS layers in behenic acid LB films were reported in detail.[1-5]

On the basis of work by Barraud's group, the process of H_2S diffusion into LB films of copper stearate and the formation of nonstoichiometric copper sulfide with semiconducting properties were studied by X-ray photoelectron spectroscopy (XPS) measurements in our lab.[6] It was shown that the reaction rate and the composition of the resulting product are both mainly controlled by the diffusion of H_2S.

Not only do LB films provide size, geometrical control, and stabilization within a single dimension for Q-state particles, they also influence the properties of the particles.[7,8] Some investigators have tried to synthesize thin layers of Q-state particles in LB films by chemical reactions.[9,10]

Recently, small particles of PbS have been prepared in several media.[11-16] It was shown that, only in poly(vinyl alcohol), a structured absorption spectrum could be obtained.[15] The absence of a structure, particularly the failure to detect the quantum size exciton peak was explained by a very broad size distribution of the particles or by the exciton peak being very broad or very weak because of a low Eg.[13,15]

We synthesized lead sulfide in the polar planes of stearic acid (SA) LB films in a method similar to that used to prepare CuS layers.[6] The composition, chemical state of Pb and S elements, and stability in air of PbS within SA LB films were studied in detail mainly by XPS.[17] It was shown that all these properties are different from those of bulk PbS and small particle PbS.

In this paper, a kind of Q-state PbS monolayer was reported. It was synthesized at a H_2S pressure of 1 Torr. By using X-ray diffraction at wide angle and IR spectroscopy, we found that PbS within SA LB films has a monolayer structure and the hydrocarbon chains of SA remain well-ordered arrays in three dimensions after the reaction. A structured UV-visible absorption spectrum on monolayer PbS is obtained. PbS monolayers do not consist of isolated monomolecular PbS. It is possible that strong quantum size effects are due to quantum wires or quantum sheets of PbS.

Experimental Section

The LB films of lead stearate ($PbSt_2$) were built up with a LB-900 trough made by us and a multicompartmental round trough from Mayer-Fein Technic Co. (Germany). The solution (in chloroform, 1×10^{-3} M) of SA was spread on a four-time distilled water subphase containing $PbCl_2$ in a concentration of about 10^{-4} M. The films were deposited (Y-type) onto a substrate (silicon, quartz, CaF_2 or glass slide) at constant surface pressure (25 dyn/cm). X-ray diffraction, XPS, scanning electron microscopy (SEM), IR and UV-visible absorption spectroscopy show that $PbSt_2$ LB films deposited under this condition have well-ordered structure in three dimensions. These results will be published in other paper.

In a vacuum system, $PbSt_2$ LB films were exposed to $H_2S(g)$ at a pressure of 1 Torr (133.3 Pa) for 12 h. All experiments are carried out immediately after the reaction except those with special explanation. X-ray diffraction patterns were obtained with diffraction vectors perpendicular to the plane of the films using a Rigaku D/max rA X-ray diffractionmeter. Thus the patterns mainly depend on the structure in the perpendicular direction to the plane of the films. IR and UV-visible spectra were taken with a Nicolet 5PC FTIR spectrometer and a Shimadzu UV-365 spectrometer, respectively.

Results and Discussion

1. X-ray Diffraction from LB Films before and after the Formation of PbS. X-ray diffraction measurement is undoubtedly a powerful method for studying order structure of materials. Many experimental and theoretical results of X-ray diffraction from many kinds of LB films have been obtained.[18-20] Especially, it

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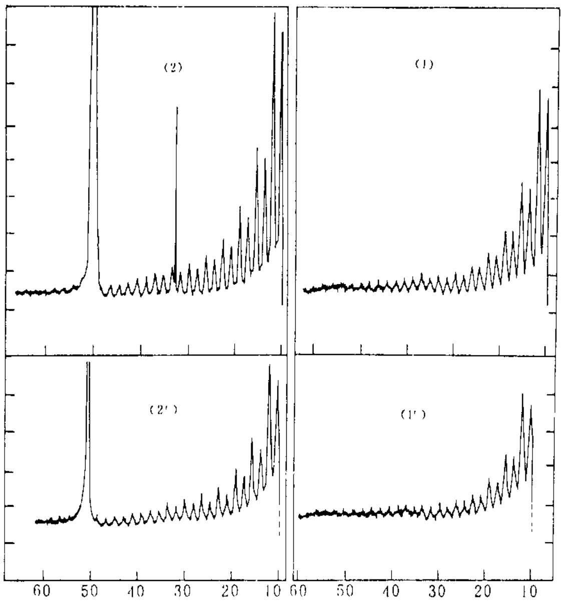

Figure 1. X-ray diffraction patterns of LB films: first line (1) five-layer $PbSt_2$ LB films, (2) seven-layer $PbSt_2$ LB films; second line (1′) five-layer SA LB films + three-layer PbS, this sample is sample 1 after the reaction, (2′) seven-layer SA LB films + four-layer PbS, this sample is sample 2 after the reaction. Both samples were deposited on quartz. All patterns were obtained under the same conditions. Peaks A and B which are respectively located at 33.0° and 50.7° are ascribed to the substrates.

was used to detect the change in the long spacing between before and after polymerization.[21,22]

Belbeoch et al. have studied the structure change of LB films of behenic acid induced by adding Ag^+ ion within the layers and further in situ reduction by X-ray diffraction at small glancing angles.[3] The magnitudes of (001) Bragg peaks of silver behenate are larger than those of behenic acid LB films. The long spacing changed from 53.50 to 58.50 Å in the first stage. After the reduction of silver, the long spacing shifted from 58.50 to 56 Å, and the diffraction pattern and the magnitudes of (001) Bragg peaks are almost the same as those of behenic acid LB films before the insertion of Ag^+ ion.

Figure 1 is the wide-angle X-ray diffraction patterns of LB films of $PbSt_2$ before (the first line) and after the reaction (the second line) with H_2S at a pressure of 1 Torr. It was shown that, after the reaction, the qualitative feature of diffraction of $PbSt_2$ LB films remains. We can distinguish peaks that are (001) Bragg peaks, before and after the reaction, all corresponding to a unit cell spacing (long spacing) 50.5 ± 0.2 Å. This is different from that mentioned above, and also different from that observed by Smotkin et al. (They observed that the average change of cadmium arachidate LB films in thickness per layer after exposure to H_2S is about 3 Å.[4]) This long spacing is much larger than that of SA LB films deposited in a general manner.[23]

It was known that the relative heights of the odd and even Bragg peaks are mostly determined by the relatively high electron density in the metal–COO group compared with the low electron density hydrocarbon chain area.[18] Thus, as a rough approximation, the unit cell of salt of fatty acid LB films can be regarded as a unit cell of metal ions.[21] That both the unit cell spacing and the qualitative feature of X-ray diffraction patterns of LB films after the reaction do not change means the lead ion unit cell does not change after the reaction, i.e. a lead ion of PbS in a LB matrix has a two-dimensional distribution. In other words, PbS generated by the reaction forms monolayers in the polar planes of SA LB films. As mentioned later, we determined that the lead ions in a polar plane of $PbSt_2$ LB films are in a single plane.

In the X-ray diffraction patterns of LB films after the reaction, there is no any new phase diffraction peak unit $2\Theta = 147°$. It was known that PbS microcrystallites still showed feature diffraction peaks of PbS even until the crystalline were as small as ca. 20 Å.[16] Thus that no any new phase peak appears can be considered as evidence for the formation of PbS monolayers.

A typical qualitative feature of a X-ray diffraction pattern of LB films is the alternation of amplitudes of the (001) Bragg peaks ($2\theta < 40°$) which is due to well-ordered arrays of hydrocarbon chains in LB films.[18] That this feature remains after the reaction revealed that hydrocarbon chains of SA still form sufficiently well-ordered arrays within LB films although they are fairly flexible. In other words, the formation of PbS does not influence the well-ordered arrays of hydrocarbon chains of LB films. This can be considered as more evidence for the formation of PbS monolayer. If three-dimensional microcrystallites of PbS formed, these microcrystallites would destroy the well-ordered arrays of hydrocarbon chains of LB films. In fact, SA LB film structure was destroyed completely (no (001) Bragg peak existed in the wide angle X-ray diffraction pattern) by PbS particles synthesized under a higher pressure (higher than 10 Torr). The size of these PbS particles determined by SEM is about 100 Å (This will be the subject of another study).

We have noticed that the amplitudes of the (001) Bragg peaks are decreased after the formation of PbS monolayer. But we have observed that 11-layer SA LB films show no (001) Bragg peaks in the wide angle region ($2\theta > 10°$) under the same conditions. Thus this decrease is different from that of the insertion of silver clusters mentioned above.[3] We considered that, in our case, it may be mainly due to the change in the election density in the polar planes of the LB films after the reaction. Although the electron numbers of the sulfur atom is much less than that of lead atom, it is obviously more than that of a carbon atom or oxygen atom.

A quantitative explanation of the X-ray diffraction patterns before and after the reaction is carried out.

2. IR Spectra of LB Films before and after the Reaction. In addition to X-ray diffraction, IR spectroscopy is also a widely used investigative tool for determining the structure of LB films.[24-26] As mentioned in the Experimental Section, the X-ray diffraction pattern of LB films obtained by the usual method mainly shows the structure in the perpendicular direction to the plane of LB films. Compared with X-ray diffraction, IR spectroscopy can conveniently provide information on the structure in three dimensions, specially on in-plane structure because it can detect intermolecular effects.[31]

The IR spectrum of SA LB films has been studied in detail.[27-29] It was observed that SA LB films have a very similar structure to that of C-form crystal and that the *a* axis (*b* axis) is parallel (perpendicular) to the dipping direction[23,24] by comparing its IR spectra with that of SA single crystals[30] and crystalline *n*-paraffins.[31] On contrary, hydrocarbon chains of salts of fatty acid LB films are packed in an orthorhombic[32,33] or triclinic fashion.[27]

Ruaudel-Teixter et al. suggested that the best analytical means for studying an inorganic reaction on LB films is IR spectroscopy, which describes the reactivity of the organic matrix and gives proof

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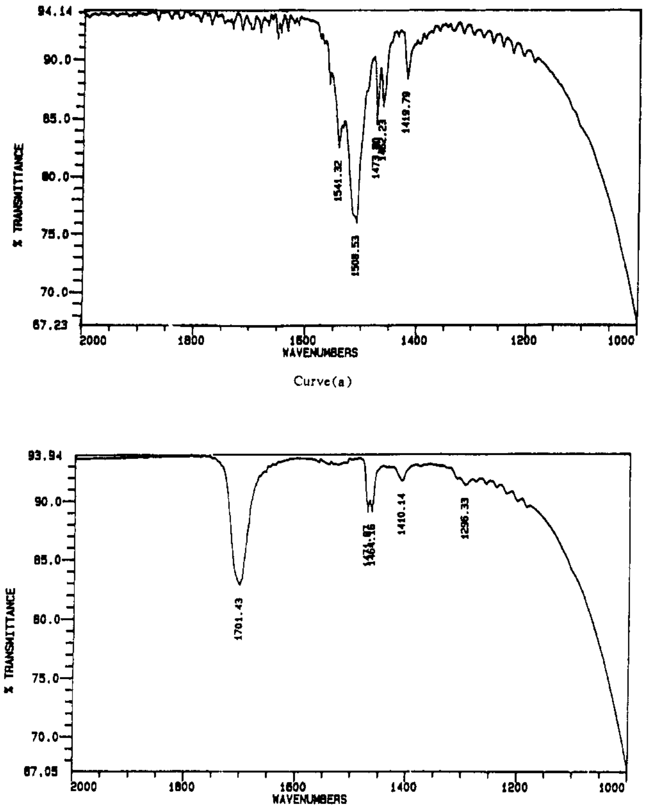

Curve(a)

Curve (b)

Figure 2. IR spectra of (a) $PbSt_2$ LB films (55-layers on each side of CaF_2 substrate). (b) SA LB films with PbS (the same sample as used in part a).

of the bonding of the diffused guest to it.[1] Using the IR method, they investigated insertion of silver into behenic acid matrix. In their case, both of the band progressions due to a trans planar structure of the long $(CH_2)_n$ sequence and the splitting of the CH_2 scissoring vibrations caused by the hydrocarbon chains being packed in an orthorhombic subcell vanished during both steps of chemical reaction.[2,4]

Figure 2 illustrates IR spectra of $PbSt_2$ LB films deposited on CaF_2 substrate before and just after the reaction.

The IR spectrum on $PbSt_2$ LB films (Figure 2, curve a) is typical of stearate salt LB films: Band progressions located at about 1150–1350 cm^{-1} consist of nine peaks;[34] a strong absorption band (asymmetric COO stretching vibration) appears at 1508 cm^{-1}, instead of a peak at about 1700 cm^{-1}. In this spectrum, there are two sharp peaks at 1474 and 1462 cm^{-1} which can be assigned to CH_2 scissoring vibrations.[31] The intensities of the two modes are strongly dependent of the direction of E (the electric vector of incidence) with respect to the dipping direction, but the dependence is not so pronounced as that of SA LB films. The 12-cm^{-1} splitting is caused by the crystal field and is characteristic of *n*-paraffins which crystallize with orthorhombic subcell packing of CH_2 groups. The COO asymmetric vibration absorption band at about 1508 cm^{-1} locates at very low frequency compared with other salts of fatty acids[35] and obviously consists of more than one peak. We considered that it is due to the formation of a dimer structure of $PbSt_2$ within LB films.[36] The well-ordered structure of $PbSt_2$ LB films in three dimensions is partly due to the dimer structure. It is the dimer structure that causes lead ions to be in a single plane in the polar planes of LB films of $PbSt_2$. From the results of X-ray diffraction, we learned that the position of lead ions does not change after the reaction. Thus PbS indeed forms monolayers in the polar planes of LB films.

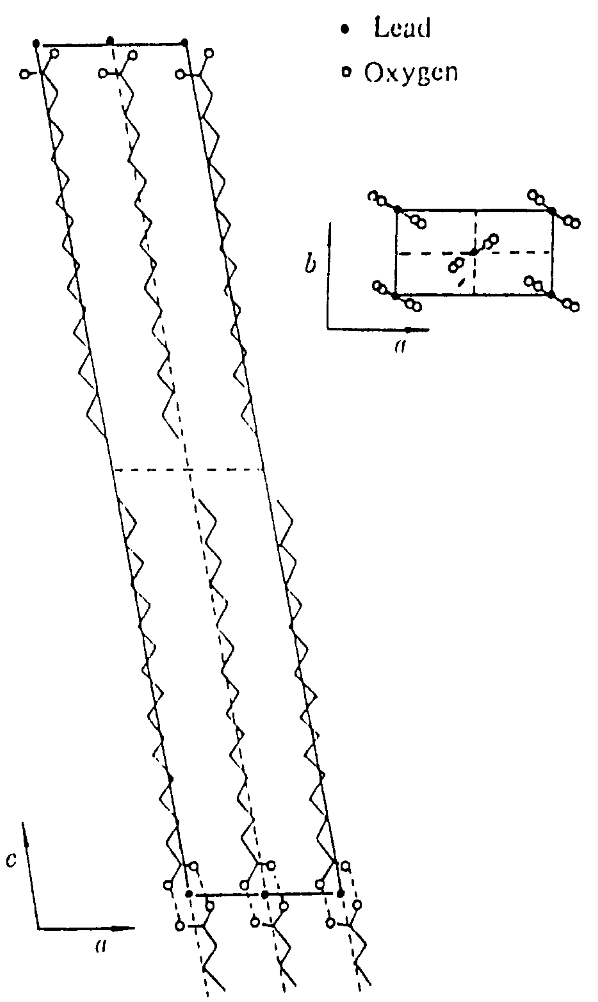

Figure 3. Structure of SA LB films with PbS generated by the reaction. The position of lead ion of PbS is shown.

The splitting of CH_2 scissoring vibrations and the band progressions remain after the reaction (curve b, Figure 2). It indicates that the hydrocarbon chains in SA LB films yielded by the reaction are still orderly packed in an orthorhombic subcell (monoclinic or orthorhombic crystal lattice). The C-form crystal of SA and SA LB films deposited in a general manner have the cell dimensions, a = 9.4 Å, b = 5.0 Å, and c = 50.7 Å and the long spacing of about 39.6 Å.[23,37] X-ray diffraction has told us that the long spacing of SA LB films yielded by the reaction is 50.5 ± 0.2 Å. This value is much larger than that of C-form crystals and LB films deposited in a general manner and very close to the value of the c axis of the single crystal. From these results, we concluded that the SA LB films generated by the reaction form an orthorhombic unit cell.

The IR spectrum of SA LB films generated by the reaction is the same as that of the C-form crystal[30] and LB films deposited in a general manner.[27,28] It means that the orthorhombic unit cell of SA LB films generated by the reaction has a similar structure to that of a C-form crystal. It has been reported that the position of the two modes of the splitting of CH_2 scissoring vibrations for orthorhombic and monoclinic crystals is the same in the case of *n*-paraffin.[31] Unfortunately, we cannot compare other absorption peaks of a C-form crystal of SA with the peaks of a SA orthorhombic one, because to the best to our knowledge, no any orthorhombic crystal has been found. This fact also indicates that SA LB films yielded by the reaction are in a metastable phase.

The band at 1701 cm^{-1} (curve b, Figure 2) is assigned to the C=O stretching vibration; the band at 1296 cm^{-1} is ascribed to the C–O stretching vibration coupled with the CO–H in-plane deformation vibration. The broadness of the later is due to the

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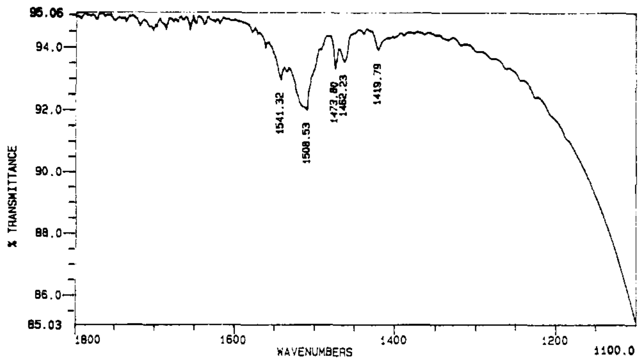

Figure 4. IR spectrum of $PbSt_2$ LB film yielded by the decomposition of PbS monolayer (15-layer $PbSt_2$ LB films on each side of CaF_2 substrate).

hydrogen bondings.[27] The lack of any carbonyl band in the "free" (C═O) region near 1745 cm^{-1} and in the sideways dimers which absorb near 1720–1730 cm^{-1} strongly implies that the hydrogen bondings are only in the ring structure (Figure 3).[38,39] (It is just the case of a SA C-form crystal.) The broadness of the C═O stretching vibration has been attributed to either the existence of two different conformations of the dimeric carboxylic acid in the unit cell[28,40] or the transition dipole–dipole coupling interactions between the C═O bands in the unit cell.[41] The existence of the ring structure of carboxylic groups is some of the most important information of the formation of PbS monolayer. It is the ring structure of the carboxylic group that provides not only geometrical control in a single plane for PbS but also an important influence for SA to keep LB film structure. Such ring structure of carboxylic groups permits the structure of PbS in the polar planes of LB films to have two possibilities:

A, monolayer: PbS is limited in a single plane by the ring structure (Figure 3).

B, cluster: In order to minimize surface energy, PbS forms clusters between the SA. Leloup et al. have found that this is the structure of the insertion of silver into behenic acid LB films and the size of the Ag cluster is as small as 10–20 Å.[2]

We have known that A is true by X-ray diffraction. Now, we can find that IR measurement also supports A, monolayer.

PbS in SA LB films synthesized under the conditions is unstable in air.[17] Figure 4 is an IR spectrum of a sample of SA LB films with PbS after its exposure to air for 86 days. This spectrum has the same absorption peaks as those of $PbSt_2$ LB films before the reaction. The very sharp splitting of CH_2 scissoring vibrations (1462 and 1474 cm^{-1}) and the band progressions reveal that hydrocarbon chains are still well-ordered after the decomposition. That every carboxylic group is shifting from COOH (1701 cm^{-1}) to COO^- (1508 cm^{-1}) indicates all lead ions are connected with COO^- again. The cluster structure (B) possibility finds it difficult to explain the decomposition. Thus we considered that the decomposition supports possibility A: PbS is limited in a single plane by the ring structure of carboxylic groups of SA LB films and each lead ion is located about one ring structure.

It has been reported that PbS small clusters (as small as monomolecule) in ethylene–15% methacrylic acid copolymer are very stable with lifetimes longer than 2 years.[10] We considered that the decomposition of PbS in LB films indicates that this kind of PbS has a special structure.

The formation of the carboxylic group ring structure implies the size of the polar planes of LB films does not change after the reaction.

3. UV–Visible Absorption Spectrum of PbS Monolayers. Because of quantum size effects of nanoparticlulate semiconductors, the UV–visible absorption spectroscopy method has become a powerful measurement to determine the structure and size of quantum confinement or quantum wells. In these nanostructures, the dimensions of the wave function of the electron–hole pair (exciton) in the lowest excited state of the nanocluster are comparable to the physical size of the particles. This quantum confinement of the exciton means that the continuum band of energies becomes more molecular in character, with narrow ranges of energy and line structure in the optical spectra.[5] In this nanostructure, the changes in the absorption spectrum of semiconductors with changing particle size are called quantum size effects. Quantum size effects make the onset of absorption shift toward short wavelength direction. The quantitative explanation of this effect in the case of the semiconductor nanoparticles has been carried out.[42-44] Thin layers of small particles of CdS have been prepared in LB films and at monolayer interfaces.[6,7] The observed range of the onset of absorption corresponded to 22–50 Å on Henglein's published E_g vs particle size curve.[42]

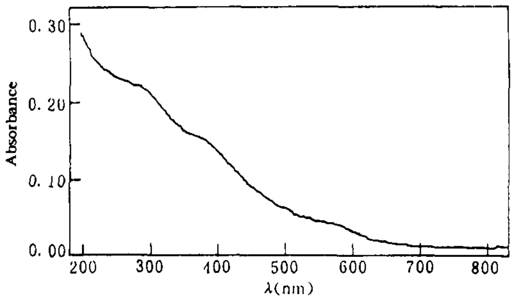

Figure 5. UV–visible spectrum of 8-layer PbS monolayers within 15-layer SA LB films on CaF_2 substrate. This spectrum was recorded just after the reaction.

The structure of PbS monolayer in the perpendicular direction to the substrate has been determined by X-ray diffraction and IR. We have obtained a little information about the in-plane structure of PbS: Each lead ion is located about a ring structure of carboxylic groups. We will find that the UV–visible spectrum can provide more information about the in-plane structure of PbS monolayers within SA LB films.

Figure 5 is the UV–visible spectrum of PbS monolayers within the SA LB films. It is shown that a structured absorption spectrum of PbS is obtained. The absorption edge of the spectrum was observed at about 690 nm, shifting about 1.4 eV with respect to bulk PbS. From these results, we can concluded that the monolayer PbS within the LB films is in a quantum confinement state (Q state).

We can find that the structured absorption spectrum of the monolayer PbS is totally different from the monomolecular PbS spectrum.[45] It implies that the PbS monolayers do not consist of isolated monomolecular PbS. Therefore, PbS monolayer should be built of PbS two-dimensional domains or PbS lines. Because the S:Pb ratio of the PbS monolayer is about 1.5,[17] these kinds of in-plane structure are possible. Considering the structure of the orthorhombic subcell of SA,[37] we guess that PbS within monolayers is linked to each other in lines along the *b* axis of the subcell (Figure 3).

The spectrum (FIgure 5) is similar to that of PbS particles in the form of rods in which strong quantum size effects occur mainly in two dimensions.[16] But the exciton peak appears at slightly shorter wavelength (580 nm).

The existence of the exciton peak in the spectrum of PbS monolayer in LB films indicates that the size of the two-dimensional PbS domains or the PbS lines is almost homogeneous.

In our case, the strong quantum size effects mainly occur in one dimension (quantum sheet) when monolayers consist of the two-dimensional domains, or in two dimensions (quantum wire)

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when PbS of the monolayer is linked to each other in lines. Thus it is not precise enough to determine the size of the quantum sheet or the quantum wire based on the hyperbolic band model or the particle-in-box model.[8]

Conclusion

PbS generated by the reaction of $PbSt_2$ LB films with H_2S at a pressure of 1 Torr forms Q-state monolayers in the polar planes of SA LB films. PbS monolayer is controlled by the carboxylic group ring structure. After the reaction, the long spacing of LB films does not change because of the formation of the carboxylic group ring structure. The hydrocarbon chains remain well-ordered arrays in three dimensions within SA LB films after the reaction. A structured UV-visible absorption spectrum with a exciton peak at 580 nm was obtained. The absorption edge shifted about 1.40 eV with respect to bulk PbS. PbS monolayer consists of the two-dimensional domains or lines, instead of isolated monomolecular PbS. Thus strong quantum size effects occur mainly in one dimension (quantum sheet) or in two dimensions (quantum wire). It indicates that low dimensional quantum wells can be obtained in LB films by chemical reactions.

Registry No. PbS, 1314-87-0; lead stearate, 1072-35-1.

An Alternating Current Impedance Model Including Migration and Redox-Site Interactions at Polymer-Modified Electrodes

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Electron hopping in redox polymer-modified electrodes requires coincident ion movement to maintain electroneutrality, and transport effects can arise due to either process. In this paper, the equation for diffusion/migration by electron hopping is used with the classical Nernst-Planck equation for mobile ionic species to rigorously model the ac impedance response of a redox-site-containing polymer attached to an electrode and bathed by a binary aqueous electrolyte. The theory also includes the effect of polymer redox-site interactions. Donnan exclusion is assumed, permitting only one mobile ion in the film. This leads to an analytical solution to the problem because the polymer can be treated as a binary electrolyte. When ion movement is slow relative to electron hopping, the impedance spectrum contains a classical Warburg region just as when electron hopping controls the rate. Although these two types of rate control cannot be distinguished from a single ac impedance spectrum, one can determine the transport controlling process from the potential dependence of the data from a series of spectra.

Introduction

About a decade ago, it was recognized that the propagation of charge through redox polymer films on electrodes frequently obeys Fick's second law. Consequently, the electron diffusion coefficient has become a characteristic parameter of charge transport through polymers on electrodes.[1,2] Because of its simplicity, use of Fick's law leads to analytical models for many electrochemical experiments. Fick's law based models have been applied to chronoamperometry,[3] cyclic voltammetry,[4] and ac impedance.[5-9]

The movement of electrons within a polymer film requires coincident transport of ions to maintain electroneutrality, and the ion-transport process can influence the overall charge propagation rate. This problem of coupled electron and ion movement has been extensively considered by Savéant and co-workers,[10-14] who first presented the modified Nernst-Planck equation that governs electron movement,[10] Buck,[15-21] and others.[22,23] Much of the work has focused on chronoamperometry. Andrieux and Savéant have shown that Cottrell behavior is observed even when ion movement is slow relative to electron hopping; the apparent diffusion coefficient is related to the diffusion coefficients of the ion movement and electron hopping processes.[14] Buck has exploited the fact that when a single ion is mobile in the film, the ion and the hopping electron compose a binary electrolyte, and a binary diffusion coefficient can be defined.[19] This binary transport is common in polymer films with a preponderance of fixed positive or negative charge; Donnan exclusion leads to low film concentrations of similarly charged mobile ions. Buck has used this approach to model the ac impedance of films sandwiched between two electrodes.[15,21] This paper establishes the analogous diffusion-migration ac impedance solution for the case where the polymer is attached to an electrode on one side and bathed in a binary electrolyte on the other. The effect of redox center repulsion/attraction and counterion activity as well as the usually small impedance contribution from the electrolyte phase are also included in the model.

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