Scanning Tunneling Microscopy and UV-Visible Spectroscopy Studies of Lead Suifide Ultrafine Particles Synthesized In Langmuir-Biodgett Films

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Ultrafine semiconductor particles of lead sulfide were synthesized by exposing lead stearate Langmuir-Blodgett films to hydrogen sulfide gas. By heating the Langmuir-Blodgett films containing PbS ultrafine particles in nitrogen gas at 120 °C for 1 h, the molecules of stearic acid were evaporated and the lead sulfide particles were left. The PbS ultrafine particles before and after evaporation were analyzed by using a scanning tunneling microscope and a UV-visible spectrophotometer.

The Langmuir-Blodgett (LB) technique is now widely used for construction of orientational organic films for which the thickness can be controlled to the precision of a nanometer (monolayer). Much attention has been paid to this technique due to the possible application in the fields of molecular electronics, optoelectronics, etc. However, much organic material has disadvantages such as the low thermal stability and mechanical stability, etc., which limit the possibility of fabricating practical nanometer devices with organic materials. Using the LB technique to assemble inorganic material provides a new approach. Our group has already fabricated ultrathin conductive graphite films by pyrolysis of photosensitive polyimide LB films¹ and synthesized ultrafine CdS particles with controllable size in polydiacetylene Langmuir-Blodgett films.²

Ultrafine semiconductor particles with nanometer size have become an increasingly interesting and important research area. With the reduction of particle size to the nanometer scale, material properties, such as optical, electrical, magnetic, electrooptical, and chemical properties, will be altered, which can be potentially exploited in a broad variety of applications.³ Many techniques have been developed to synthesize ultrafine semiconductor particles in the nanometer regime in a variety of media, such as polymers,⁴ thin films,⁵ glasses,⁶ solutions,⁷ monolayers,⁸ and zeolites.⁹

We report here the synthesis and analysis of PbS ultrafine particles in lead stearate Langmuir-Blodgett films. By exposing the LB films of lead stearate to hydrogen sulfide gas, the PbS particles can be generated in the films. The generation of PbS ultrafine particles were determined from UV-visible spectra. After the LB films containing PbS particles were heated in nitrogen gas at 120 °C for 1 h, the molecules of stearic acid were evaporated and the PbS particles were left. The PbS particles on graphite were then analyzed by the scanning tunneling microscopy (STM).

Multilayers of lead stearate were deposited on graphite and quartz substrates by LB method as follows: The monolayer was prepared in a Langmuir trough by spreading a 1×10^{-3} M solution of stearic acid in chloroform on subphase of distilled water containing 4×10^{-4} M of Pb(NO₃)₂. The stearic acid molecules reacted upon lead ions in the subphase as follows:

 $2CH_3(CH_2)_{16}COOH + Pb^{2+} \rightarrow$

$$[CH_3(CH_2)_{16}COO]_2Pb + 2H^+$$

Well-cleaned quartz (chromic acid, dust-free water) and highly oriented pyrolytic graphite (HOPG, freshly cleaved) were used as substrates for absorption spectrophotometry and scanning tunneling microscopy, respectively. The substrate was moved across the monolayer on the aqueous subphase to build up lead stearate LB films, at velocity of 5 mm/min for the first layer and



Figure 1. UV-visible spectrum of (A) lead stearate LB films and (B) stearic acid LB films containing PbS ultrafine particles.

15 mm/min for the following upward and downward, at constant surface pressure of 30 dyn/cm, 20 and 41 layers of lead stearate were built by the above procedure on HOPG and quartz, respectively.

After the buildup, the lead stearate LB films were then air-dried and exposed to hydrogen sulfide gas for 24 h. Lead stearate reacts with hydrogen sulfide as follows:

$$[CH_{3}(CH_{2})_{16}COO]_{2}Pb + H_{2}S \rightarrow 2[CH_{3}(CH_{2})_{16}COOH] + PbS$$

Evidence for PbS formation between the head-groups of the LB films was obtained by UV-visible absorption spectra. The spectra were taken before (Figure 1a) and after (Figure 1b) the exposure to the hydrogen sulfide gas with a Beckman DU-8 spectrophotometer. The absorption peak at 250 nm in Figure 1 represents the characteristic absorption band of lead stearate. After exposure, the spectrum shows an absorption edge at about 540 nm (the intersection of the base line with the tangent drawn to the absorption shoulder). This represents the generation of the semiconductor of PbS. The observed absorption edge is blue shifted from that of bulk PbS, which is about 3000 nm. This is due to the quantum size effect of ultrafine particles with nanometer size. The observed absorption edge led to an assessment of about 1.5 nm for the mean diameter of the PbS particles from Wang's published absorption edge vs particle size curve.³

After the LB films containing PbS particles on HOPG were heated in nitrogen gas at 120 °C for 1 h, molecules of stearic acid were evaporated and PbS particles were left on the substrate.



Figure 2. Scanning tunneling microscopic (STM) image of PbS on graphite. The right side shows the graphite substrate. The size of the image is 2.8 nm × 2.3 nm.



Figure 3. STM images of PbS on graphite with sizes of (top) 188 nm \times 132 nm and (bottom) 25 nm \times 18 nm.

Scanning tunneling microscopic images were then acquired by means of a Nano-Scope I (Digital Instruments, Inc., Santa Barbara, CA) operated in the constant-current mode. A platinum wire was used for the tunneling tip. Images were scanned with 20 lines/s 30-mV tip bias. All of our tunneling images were obtained in air at room temperature. To ensure that the STM was operated optimally, we would first scan the graphite surface under conditions which allowed us to resolve atomic features on the graphite surface. Figure 2 shows the edge of PbS layer on graphite surface. From the image, we can resolve the atoms of graphite with diameter of 0.25 nm. Then we would scan over the surface of the PbS laver.

Figure 3a displays the typical appearence of a PbS-particlecovered HOPG surface scanned by the STM. The large scale scan reveals a stripe structure. The stripes are parallel to each other in a small domain and change direction in another domain. As shown in Figure 3b, every stripe consists of ultrafine particles with diameters from 1.0 to 2.0 nm. The stability and brightness



Figure 4. STM image of PbS monolayer on graphite spaced by stearic acid monolayer. The size of the image is $6.3 \text{ nm} \times 5.6 \text{ nm}$.

of the STM images indicate the presence of semiconductor particles strongly adsorbed on the HOPG substrate. The stripe structure might be caused by the penetration of hydrogen sulfide gas into the LB films and the evaporation of stearic acid from the films.

To obtain the image before evaporation, we prepared one monolayer of lead stearate on HOPG and exposed it to hydrogen sulfide gas to generate PbS. Since the graphite is hydrophobic, a horizontal diposition method¹⁰ was used to transfer a single monolayer of lead stearate to HOPG with the hydrophilic head (-[COO]₂Pb) contacting air. Figure 4 shows the appearance of PbS on graphite spaced by the monolayer of stearic acid. We found that images of this kind of sample are not stable. It might be caused by two reasons. One is the weak adsorption of PbS on stearic acid monolayer. Another one is the presence of the insulating monolayer of stearic acid which separates PbS molecules from the graphite surface by about 2.5 nm. Nevertheless, it is found that the PbS monolayer is not homogeneous, and molecules of PbS formed aggregates on the monolayer of stearic acid.

In conclusion, we have synthesized PbS ultrafine particles with mean diameter of about 1.5 nm in stearic acid LB films and analyzed them using scanning tunneling microscopy and UVvisible spectroscopy. After evaporating stearic acid molecules, we can obtain stable high-quality STM images of PbS layer. The size of PbS particles observed from STM image ranged from 1.0 to 2.0 nm, which is identical with the assessment from UV-visible spectroscopy. For PbS monolayer spaced by a monolayer of stearic acid on graphite, the STM image was not stable and the monolayer of PbS is not homogeneous.

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