A Monolayer of PbI_2 Nanoparticles Adsorbed on MD–LB Film

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PbI_2 nanoparticles have been successfully assembled into a monolayer structure by a new method combining Langmuir–Blodgett (LB) techniques and the molecular deposition (MD) method; the stabilisation effect of the LB–MD film can prevent the nanoparticles from aggregating further after being deposited.

Recently, the study of semiconductor nanoparticles has received increasing attention.[1,2] Reducing the particle size to nanometres alters electrical, magnetic, electrooptical and chemical properties.[2] To organize the semiconductor nanoparticles in an orderly fashion in a matrix may provide a potential application of these special properties. Many matrices have been used for organising semiconductor nanoclusters into a layer structure such as LB films (LB = Langmuir–Blodgett),[3–9] and casting multilayer films.[10] Here the study of a PbI_2 nanoparticle monolayer formed on the MD–LB (MD = molecular deposition) film is presented.

The MD film was made by electrostatic attraction between opposite charges from different bipolar molecules.[11–13] The MD method is a simple and effective approach to building ultrathin organic, polymeric, organic inorganic nanoparticle alternate films, and is not limited by the shape or size of the substrates. Substrates covered with LB films were used during the molecule deposition process. Firstly, two layers of Y-type LB film of stearic acid (St) were transferred onto some hydrophilic substrates, then one layer of bipolar pyridinium was adsorbed onto the carboxylic surface of the St–LB films, lastly, one layer of anionic PbI_2 was deposited after the bipolar pyridinium (Fig. 1). Substrates such as Si, CaF_2, quartz, glass, Ag, Au are widely used for LB films, so LB film-covered substrates can provide a wide range of substrates for MD films.

In order to observe the PbI_2 nanoparticles monolayer in this MD film with TEM, a copper grid covered with a very thin layer of Formvar was used as the LB film substrate.

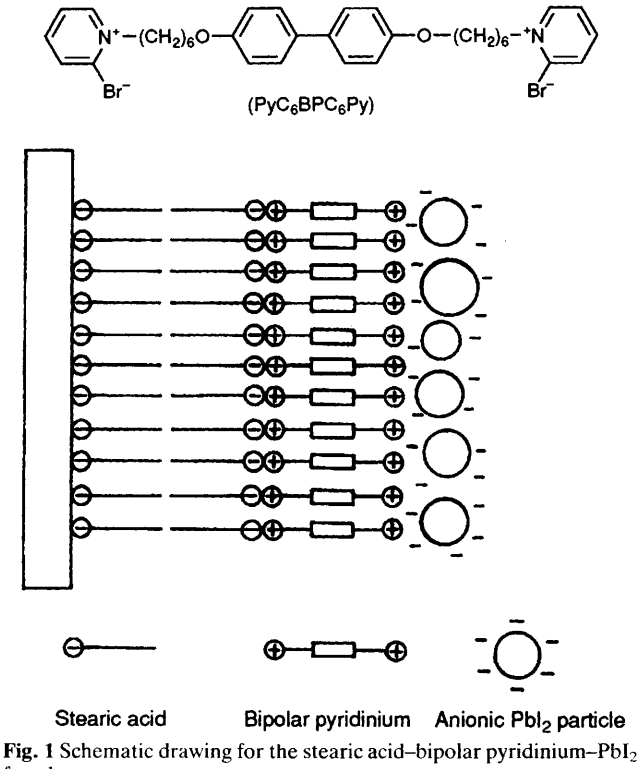

Fig. 1 Schematic drawing for the stearic acid–bipolar pyridinium–PbI_2 four layers structure

The PbI_2 nanoclusters used were prepared as reported.[14] In the absence of stabiliser agents, colloids of lead iodide were prepared in water at room temperature. Typically, 5 ml of a 0.01 mol dm^{-3} aqueous solution of lead nitrate was added to 100 ml water. The solution was then vigorously stirred as 2.5 ml of the 0.05 mol dm^{-3} aqueous potassium iodide was rapidly injected by syringe. With the molar ratio between I^- and Pb^{2+}

Fig. 2 Photograph of the monolayer PbI_2 nanoparticles deposited on MD–LB films, the magnification is 200 000

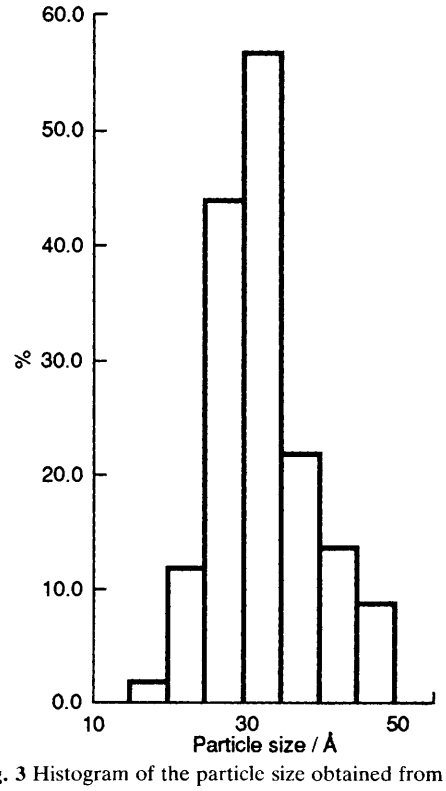

Fig. 3 Histogram of the particle size obtained from Fig. 2

a little larger than the two in water, anionic PbI_2 hydrosol was obtained. A bipolar pyridine salt **1** was synthesized and used as the cationic part for the organic inorganic alternating films.

The copper grid covered with a thin layer of Formvar was formed by dropping Formvar chloroform solution (0.5% mass) onto pure water. The solution spread rapidly. After evaporation of the solvent, a very thin Formvar film formed. A copper grid covered with this thin film was obtained and used as the LB film substrate. Two layers of stearic acid Y-typed LB films were transferred onto the hydrophilic side of the Formvar film on the copper grid at a constant surface pressure of 25 mN cm^{-1} at 20 °C. The copper grid was then covered with a thin layer of Formvar and two layers of stearic acid LB films, and immersed into a 5 mg ml^{-1} of bipolar pyridine salt solution (pH = 8). In this way, one pyridinium layer was added to the carboxylic surface while giving an opposite surface charge. After washing with deionized water and drying, it was dipped into 0.5 mg ml^{-1} of PbI_2 hydrosol for 30 mins absorbing one layer of PbI_2 nanoclusters on the pyridinium film. Using CaF_2 instead of the copper grid, a multilayer could be obtained by repeating the procedures using PbI_2 hydrosol solution and the bipolar pyridine salt solution.

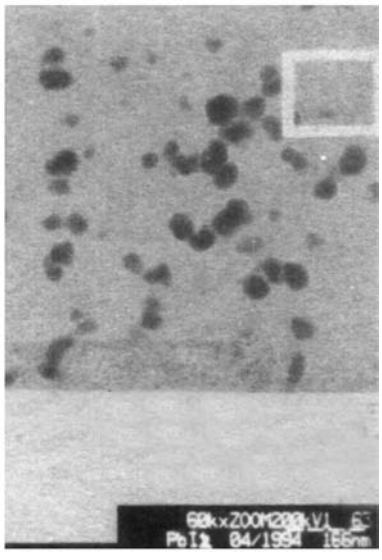

Fig. 4 Photograph of the anionic PbI_2 particle from PbI_2 hydrosol. The magnification is 60 000. One droplet of the hydrosol was directly dripped onto the copper grid which was covered with a thin layer of Formvar, then was blown dry with N_2 during the TEM sample preparation. It can be seen that in the square frame there are many small particles which are much smaller than the large one.

From a photograph of the monolayer PbI_2 nanoparticles deposited on the MD–LB film, Fig. 2, the average particle size was found to be 38 Å. Almost all the PbI_2 particles are round and close packed, but they do not form large aggregates. The same result has been obtained after the sample for TEM detection had been kept dry for 10 d. In preparing the TEM sample, one droplet of anionic hydrosol was directly dripped onto the copper grid covered with a thin layer of Formvar and then blown dry with N_2. From Fig. 4, it can be seen that the particle size of the PbI_2 is much larger than that in Fig. 2. The size of large particles are 33–70 nm, but in the inset there are still many small particles which implies that the small particles had aggregated into large ones during the evaporation in the sample preparation. this proves that the bipolar pyridinium film can effectively keep the small particles from growing further.

This work was supported by the National Science Foundation. The contributions by Dr Yu, S. and Liu, Y. L. are gratefully acknowledged.

Received, 7th July 1994; Com. 4/04141K

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