Constructing PbI_2 Nanoparticles into a Multilayer Structure using the Molecular Deposition (MD) Method

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MD films are adopted as matrices for the assembly of PbI_2 nanoparticles into a layer structure; UV–VIS and X-ray diffraction results prove that the multilayers formed have a well-defined layer structure.

Because of potential applications in molecular or supramolecular devices, the organization of semiconductor nanoparticles into layer structures has received increasing attention. LB films (LB = Langmuir–Blodgett) and casting multilayer films have been used as matrices in fulfilling such organization by many groups worldwide.[1–9] Here we report a new matrix using molecular deposition (MD) films.

Organic ultrathin films are assembled by the MD method *via* electrostatic attractions between oppositely-charged species.[10] The thermal and long-term stability of the MD films are greatly improved compared with films formed by other methods. As a dependable organizing method, it has been reported in detail elsewhere.[11,12] Using this method, some functional molecules such as enzymes and semiconductor nanoparticles have been easily organized into layer structures.[12,13] The organization of semiconductor quantum dot materials such as PbI_2 nanoparticles has been accomplished in our laboratory. In this paper, further results about organic–inorganic alternating multilayers are reported. The experimental results showed a well-defined layer structure of the multilayers.

The PbI_2 nanoclusters used were synthesized *via* the method of Sandroff *et al.*[14] The PbI_2 hydrosol was prepared in the absence of stabilizer agents at room temperature. Typically, 5 ml of a 0.01 mol dm^{-3} aqueous solution of lead nitrate was added to 100 ml water. This solution was then vigorously stirred as 2.5 ml of a 0.05 mol dm^{-3} aqueous potassium iodide solution was rapidly injected by syringe. The anionic PbI_2 hydrosol was obtained from this process by keeping $[I^-]$ at a slightly higher level than that required for a 2 : 1 $[I^-]:[Pb^{2+}]$ ratio in the solution. The bipolar pyridinium salt (pyC_6BPC_6py) **1** was synthesized and used as the cationic species.

The deposition process is described as follows. Firstly, a hydroxylated substrate (quartz or silicon) was prepared to react with the vapour of 3-aminopropyltriethoxysilane in xylene, so that it was modified with one layer of aminopropylsilane.[15] This substrate was fully protonated by being dipped into 0.01 mol dm^{-3} HCl, dried and then immersed in 0.5 mg ml^{-1} PbI_2 hydrosol (pH 5–6) for 30 min, thus covering the substrate with a layer of PbI_2 nanoclusters. After washing with deionized water and drying, the substrate was transferred into a 0.5 mg ml^{-1} bipolar pyridinium salt solution (pH 5–6). In this way, the second layer of the bipolar pyridinium was added while restoring the original surface charge. The multilayer result was obtained through repeating the above procedure using the PbI_2 hydrosol solution and the bipolar pyridinium salt solution.

The UV–VIS spectra (Fig. 1) of the multilayer films were recorded on SHIMADZU MPC-3100. The insert clearly shows a linear relationship between the absorbance of the multilayers at different wavelengths and the number of layers present, which indicates the vertical periodic structure of the organic–inorganic alternating films. At the same time, extra-

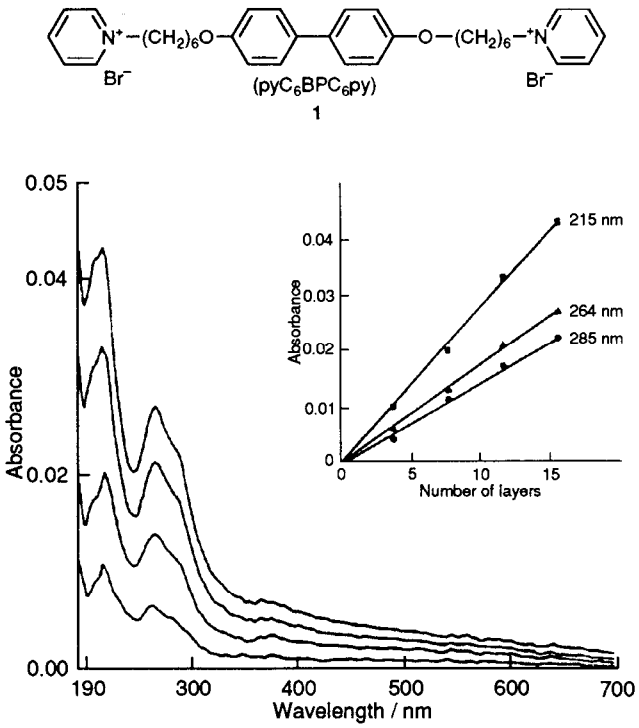

Fig. 1 UV–VIS spectra of alternating MD films of PbI_2 nanoparticles and bipolar pyridinium with: (*a*) 4; (*b*) 8. (*c*) 12; and (*d*) 16 layers. Insert: Absorbance *vs.* number of layers at 215, 264 and 285 nm

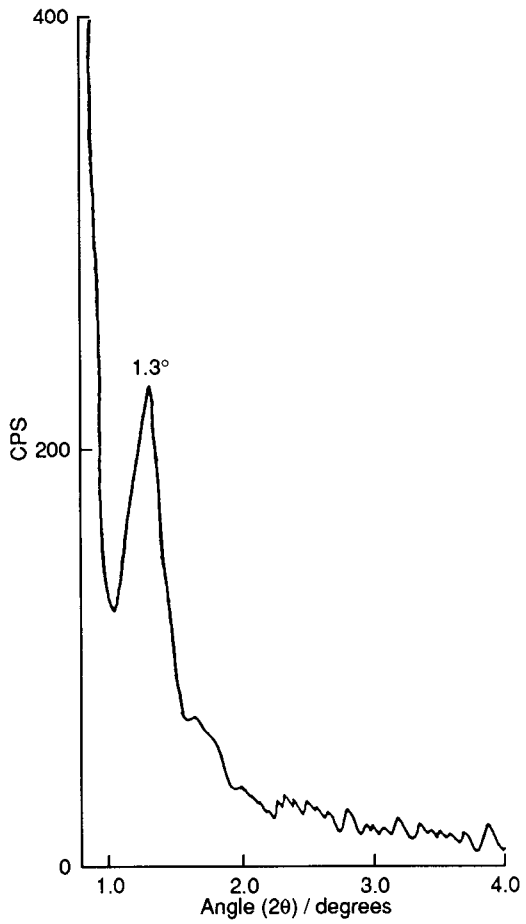

Fig. 2 X-ray diffraction spectrum of 20 layers of PbI_2 nanoparticles and bipolar pyridinium alternating MD films

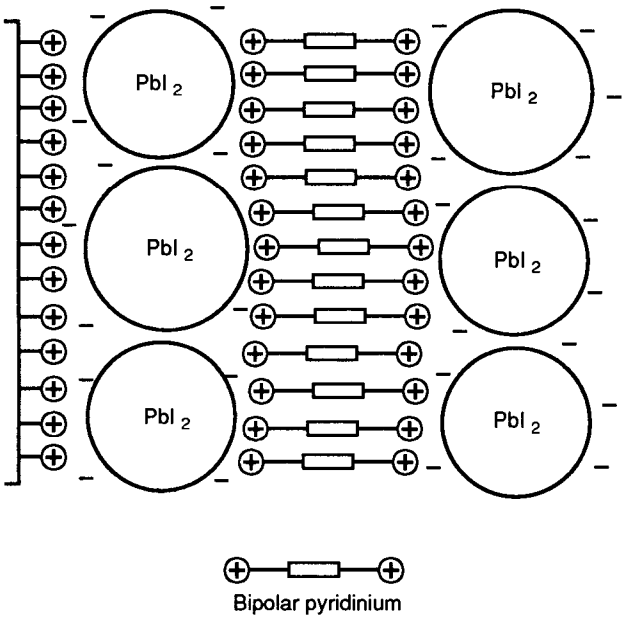

Fig. 3 The proposed structure of the multilayer alternating films

polation of the linear lines passes through, or very close to, the zero point, which proves the monomolecule-layer deposition process.

Another proof for the multilayer structure was obtained from an X-ray diffraction study, Fig. 2. The diffraction peak was identified as the first level diffraction peak of the multilayer structure. The *d*-spacing calculated by the Bragg equation was 6.7 nm.

The average particle size was found to be 38 Å (TEM), while the thickness of one layer of bipolar pyridinium is about 3 nm, which is to say the long period distance of the multilayers is about 6.8 nm. This is in good agreement with the X-ray diffraction results, and proves that PbI_2 did not aggregate in the vertical direction during the deposition process, which guaranteed monomolecule-layer deposition. Fig. 3 shows the proposed structure of the multilayer.

In conclusion, a new matrix has been adopted for the organization of semiconductor nanoclusters into a multilayer structure. The strong electrostatic attraction between the anionic and the cationic parts guarantees a very good layer structure of this new kind of organic–inorganic alternating film. Owing to the special physical and chemical properties of the semiconductor nanoparticles, this kind of structure may have a wide range of applications, *e.g.* in the fields of non-linear optics and electron transfer, for the 'wet' colloid.

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