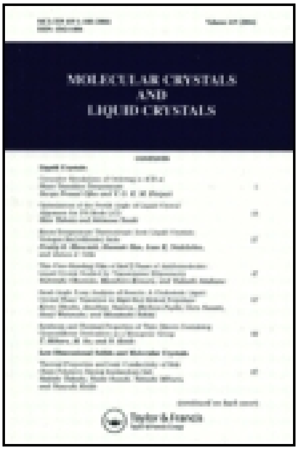

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Langmuir-Blodgett Film Formation from Surfactant-Capped Zinc Sulfide Nanoparticles Spread on Water Surface

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The surfactant-capped ZnS nanoparticulate multilayer film has been fabricated by Langmuir-Blodgett(LB) technique. ZnS LB film was investigated by the small-angle x-ray diffraction(XRD), atomic force microscopy(AFM) and transmission electron microscopy(TEM). The results indicate that ZnS nanoparticulate LB film is one-dimensional superlattice.

Keywords: Langmuir-Blodgett film; zinc sulfide

INTRODUCTION

During the last ten years there has been a growing interest in the fabrication and characterization of semiconductor nanoparticles embedded in an insulating matrix[1]. A variety of methods have been used to generate semiconductor nanoparticles in various media. However, recently the growth of chalcogenide particles in a LB film matrix has attracted a great deal of interest. Fendler *et al.*[2] have reported the fabrication of surfactant-capped CdS nanoparticulate LB film. As continuation and development of this work, in this paper, we report the transfer of sodium hexametaphosphate(Na-HMP) stabilized ZnS particles from water into apolar organic solvent(chloroform) by dioctadecyldimethylammonium bromide(DODAB) and formation of nanoparticulate surfactant-capped ZnS nanoparticles film on water surface. Further, the nanoparticulate films were transferred, layer-by-layer, from the water-air interface onto solid substrates to yield a stable ultrathin ZnS semiconductor superlattice.

EXPERIMENT SECTION

Aqueous ZnS nanoparticles base sol was prepared by the established procedure[2], in which $Zn(NO_3)_2$ and thioacetamide were used to replace $Cd(ClO_4)_2$ and H_2S respectively. The pH of this solution was adjusted to 9.5.

Nanoparticulate layers were transferred onto solid substrates (quartz for XRD, mica for AFM, copper grid for TEM) using KSV5000 system at surface pressure of 20mN/m. Z-type multilayer was produced. Overall transfer ratios were 1.0±0.1. XRD was taken with Rigaku D/max RA X-ray diffractionmeter by Cr radiation. AFM measurements were performed on a Nanoscope IIIa(Digital instruments Inc.) with contact-mode AFM. TEM studies were carried out with JEOL-2100 electron microscope.

RESULTS AND DISCUSSION

H_2S was usually used to prepare chalcogenide nanoparticles. Due to the poison of H_2S, this experiment was improved by using thioacetamide instead of H_2S. Through the hydrolysis of thioacetamide, S^{2-} was produced gradually and uniformly. It not only assisted in achieving smaller nanoparticles with narrower size distribution but also makes the experiment easier to control.

The ZnS nanoparticles, prepared initially in aqueous solutions, were stabilized by Na-HMP. This polyanion terminated the crystal growth by electrostatic attachment on the ZnS nanoparticulate surface. Equally importantly, it provided negative surface charges and thereby maintained the

ZnS nanoparticles in the aqueous dispersion solution. Positively charged longchain DODAB molecules were attracted to the available anionic sites, which rendered the ZnS nanoparticles hydrophobic. So those were extractable into apolar solvent. The nanoparticles extracted into chloroform solvent may be perceived as a kind of reversed micelles whose cores were the hexametaphosphate-stabilized ZnS nanoparticles.

Capped ZnS nanoparticles can be spread on the water surface. Surface pressure(π) vs surface area(A) isotherm was recorded on KSV5000 system. DODAB-capped ZnS nanoparticles formed a stable monolayer on the water surface, which underwent liquidlike state(π<15mN/m) to condensed state(π>15mN/m) transition and collapsed at π=35mN/m. Because it is hard to determine the concentration of ZnS nanoparticles, from the π-A isotherm, we can not know the area per DODAB-capped ZnS particles.

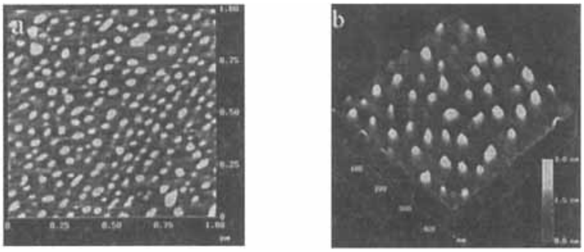

FIGURE 1 The two-dimensional (a) and three-dimensional (b) AFM images of DODAB-capped ZnS nanoparticulate LB film.

AFM images can provide two-dimensional and three-dimensional information on the nanoparticulate layer of the DODAB-capped ZnS nanoparticles. The ZnS particles are seen to be evenly distributed with little aggregation of the particles and partially ordered arrangement. AFM images show that DODAB-capped ZnS nanoparticles are not densely arranged. It indicates that DODAB molecules occupy the space among nanoparticles.

The size and micrograph of ZnS nanoparticles are shown in Fig. 2. TEM image shows that the particles are uniform in size. The size of particles is ca. 200Å. The distribution and arrangement of particles are consistent with the results of AFM.

The X-ray diffraction pattern of the 69-layer DODAB-capped ZnS nanoparticulate LB film is shown in Fig. 3. There is only one peak corresponding to (002) Bragg order that indicates layered structure with bilayer spacing of 180 Å. Because DODAB-capped nanoparticles are not densely arranged, Inter-multilayer nanoparticles should be cross-arranged, therefore, the bilayer spacing is less than the average diameter of nanoparticles. The results of TEM totally match with those of AFM. So the 69-layer DODAB-capped ZnS nanoparticles film is considered as one-dimensional superlattice.

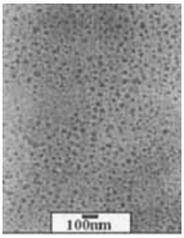

FIGURE 2 The TEM image of DODAB-capped ZnS nanoparticulate film.

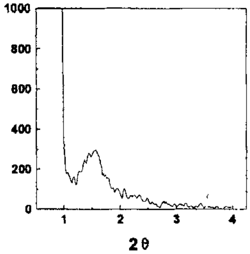

FIGURE 3 XRD spectra of 69-layer DODAB-capped ZnS nanoparticulate LB film.

Acknowledgments

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