

Nanostructured Lead Sulfide Containing Nanoholes Templated by Lyotropic Hexagonal Liquid Crystals

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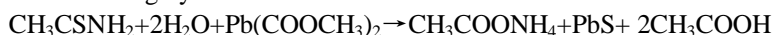
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Abstract: The hexagonal liquid crystal mediated synthesis of nanostructured PbS was studied. Thioacetamide and lead acetate were used as the sulfide and lead source, respectively. It was found that the nanohole structure of PbS was formed in this system.

Keywords: Hexagonal liquid crystal, nanomaterial, lead sulfide.

Ordered nanostructures such as nanoparticle superlattices, nanowire arrays, and mesoporous molecular sieves are expected to exhibit extraordinary properties¹⁻³. Therefore the preparation of such structures is attracting great attention^{1,3,4}. The template directed synthesis is particularly important because it can perform a good guidance to the whole reaction procedure³⁻⁶. Lyotropic hexagonal liquid crystals have been widely used as the synthesis templates for mesoporous materials⁶ since the Mobil group reported their work in 1992^{7,8}. Recently, the hexagonal liquid crystal systems were also adopted to the preparation of other nanostructures. Stupp and Braun *et al.* reported the synthesis of semiconductor-organic superlattices based on CdS and CdSe templated by hexagonal liquid crystals^{3,9}. They also synthesized the semiconductor films punctured with a regular array of holes based on CdS and CdTe templated still by hexagonal liquid crystals^{10,11}. The films can be used as molecular sieves, molds for preparing nanowire arrays, and high efficiency solar cells¹⁰. We have reported the synthesis of ZnS and CdS nanowires in the hexagonal liquid crystal media^{12,13}. We prepared nanostructured PbS containing ordered nanoholes in the similar media in the present work.

C₁₆₋₁₈EO₇ (Henkel) is purchased. All other chemicals are of analytical reagent grade. 1.00 mL aqueous solution of 0.10 mol/L lead acetate and 0.50 mol/L acetic acid, 1.00 mL of 0.10 mol/L thioacetamide, and 2.00 mL of C₁₆₋₁₈EO₇ were mixed thoroughly. The viscous mixture was aged at room temperature for two days, and the mixture turned from colorless to dark gray. The reaction was as follows:



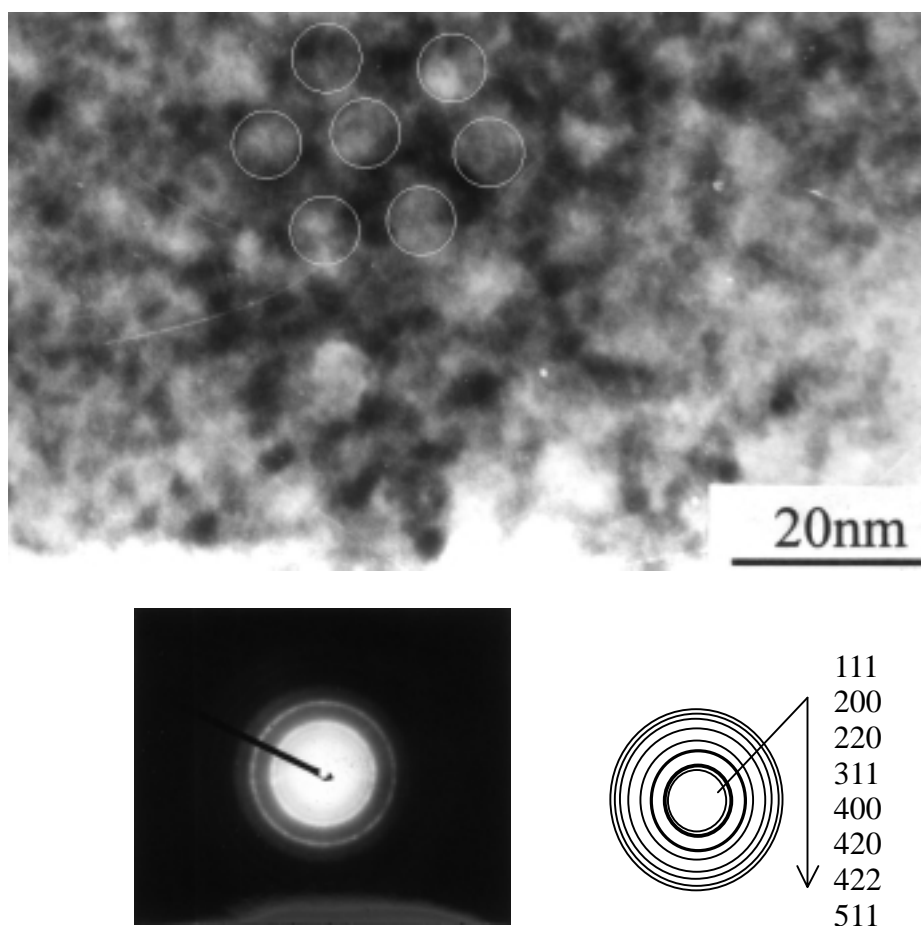
The structure of the reactive and productive mixture was investigated with a Leitz Laborlux 12 Pol Polarization Microscopy and a Rigaku D/MAX2000 X-Ray Diffraction Meter. The productive mixture was dispersed in ethanol, dropped on the copper grids,

and observed under a JEM-200CX Transmission Electron Microscopy.

The reactive mixture presented a fan-shaped texture under the polarized microscopy. This indicates that the sample is of the hexagonal liquid crystal structure.

It was found that the X-ray diffraction patterns of the reaction at the beginning and after two-days' aging are very similar. This indicates that the system maintains its hexagonal package during the reaction process. We can calculate out that the diameter of the surfactant cylindrical assemblies is 10.3 nm, the distance between the centers of neighboring cylinders is 11.3 nm.

Figure 1 The TEM image and the electron diffraction pattern of the product

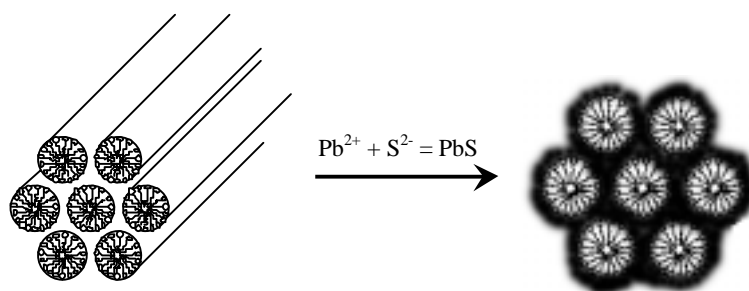


The TEM image of the product and the electron diffraction pattern were shown in **Figure 1**. Many holes with the sizes of about 5 to 8 nm were found. The distance between them is about 10 to 13 nm. The distance is in accordance with that between the cylindrical assemblies of the surfactants. But the holes are smaller than the cylinders. The

electron diffraction result shows clearly that the nanostructured material is lead sulfide with zinc blende structure. The assignment of the diffraction ring was denoted in the figure.

From the above results we can deduce the probable mechanism for the formation of the nanoholes: The reactants exist in the aqueous phase. Therefore the reaction will take place in this part and result in the nanohole structure. But Pb^{2+} ions were also located at the hydrophilic part of the surfactant molecules due to the coordination interaction, and the PbS can also form in this part. Thus the holes will be smaller than the cylindrical surfactant assemblies. The schematic diagram of formation of lead sulfide containing nanoholes is clearly shown in **Figure 2**.

Figure 2 The formation process of lead sulfide containing nanoholes with hexagonal liquid crystal as synthesis template.



H_2S , Na_2S or $(\text{NH}_4)_2\text{S}$ are normally used as the sulfide source in the synthesis of sulfide nanomaterials with solution chemistry methods. They will bring the problems of heterogeneous mixing and the interference to the structure of the reaction media. This may be the reason why mesoporous sulfide compounds are very difficult to synthesize. In this study, we selected thioacetamide as the sulfide source. It can gradually liberate H_2S in aqueous condition. This will be very effective to eliminate the above problems, and lead to the formation of nanohole structures. The nanostructured PbS containing ordered nanoholes is expected to present some special properties.

Acknowledgment

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