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研究简报

双连续微乳体系中PbS纳米管的控制合成

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Controlled Synthesis of PbS Nanotubes in Bicontinuous Microemulsion System

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Abstract: PbS nanotubes were synthesized by the tiny water channels in bicontinuous microemulsions consisted of *p*-octyl polyethylene glycol phenylether (OP)/*n*-amyl alcohol/cyclohexane/water. The possible formation mechanism of PbS nanotubes is also discussed based on their shape evolutions. The results indicate that the formation of PbS nanotubes is probably via the process of the nucleation, growth, assemblage and crystallization.

Key words: controlled synthesis; PbS; nanotubes; bicontinuous microemulsions

0 Introduction

In the past decades, there has been much interest in the synthesis and characterization of PbS nanoparticles due to their fundamental physical properties as well as their potential applications [1]. Therefore, PbS nanoparticles with different morphologies have been prepared using a variety of methods such as dendritic nanostructures by ultrasonic method[2], hollow nanospheres by sonochemical method[3], flower-shaped structure by a hydrothermal process [4], cross-shaped nanostructures by a surfactant-assisted reflux process[5], nanocrystals in ethanol by a microwave heating synthesis[6], and hollow cubic nanocrystals by controlling the reaction temperature of the hydrothermal reaction[7]. However, the synthesis of PbS nanotubes is especially difficult. Therefore, more and more efforts have been devoted to develop novel synthetic routes for PbS nanotubes.

Of synthetic methods, microemulsion method has been popular for the synthesis of nanoparticles with different morphologies. This method bears several advantages compared to others: it is a soft chemistry method, demanding no extreme pressure or temperature control, and requiring no special nor expensive equipment. However, because of the complexity of microemulsions interior structure[8-9], it is necessary to investigate the formation mechanism of nanoparticles in microemulsion systems, which has not been well established yet. Though the tiny water channels in the

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bicontinuous microemulsion are useful soft templates, few people used it as an effective crystal growth modifier. To the best of our knowledge, no report has thus far been available by using bicontinuous microemulsion as a medium for synthesis of nanotubes. We have worked on bicontinuous microemulsion as a medium during the past years. Previously, various shapes of $CaCO_3$[10] and CaC_2O_4[11]nanocrystals, such as solid sphere, network, whisker, rod, hollow sphere, and butterfly-like ones were prepared in bicontinuous microemulsions in our research group. We report here our current work in the synthesis of nanotubes. A microemulsion method was developed to obtain PbS nanotubes by the tiny water channels in bicontinuous microemulsions consisted of *p*-octyl polyethylene glycol phenylether(OP)/*n*-amyl alcohol/cyclohexane/water.

1 Experimental

The bicontinuous microemulsion system was prepared by adding in sequence of 10.00 mL of cyclohaxane, 6.00 mL of OP, 2.50 mL of *n*-pentanol and 10.00 mL of 0.01 mol·L^{-1} $Pb(CH_3COO)_2$ solution. The same experiment was also performed by replacing 0.01 mol·L^{-1} $Pb(CH_3COO)_2$ solution with 0.05 mol·L^{-1} Na_2S solution. Then the above two microemulsions, one containing Pb^{2+} and the other containing S^{2-}, were mixed quickly followed by shaking for another 1 min. The mixture was aged at room temperature for 4 d. The solid products were separated by centrifugation and further washed with acetone, absolute ethanol and distilled water for three times, respectively. Then these products were dried at the room temperature for further characterization.

XRD patterns were recorded using a MAC Science Co. Ltd. MXP 18 AHF X-ray diffractometer with graphite monochromatized Cu $K\alpha$ radiation (λ =0.154 056 nm). The accelerating voltage and applied current were 40 kV and 100 mA, respectively. TEM images were taken with TEOL-TEM-100sx transmission electron microscope. The microemulsions containing the products were deposited onto carbon film supported by copper grids and evaporated in air at room temperature.

2 Results and discussion

Fig.1 shows the XRD pattern of PbS sample synthesized in bicontinuous microemulsion system. All the diffraction peaks can be indexed to the face-centered cubic phase of PbS with lattice constant a=0.593 4 nm, which is in good agreement with the literature value of a=0.593 6 nm(PDF No.5-592). The major seven peaks can be indexed as 111, 200, 220, 311, 222, 400, and 331, respectively. No impurity phases could be detected in the XRD pattern.

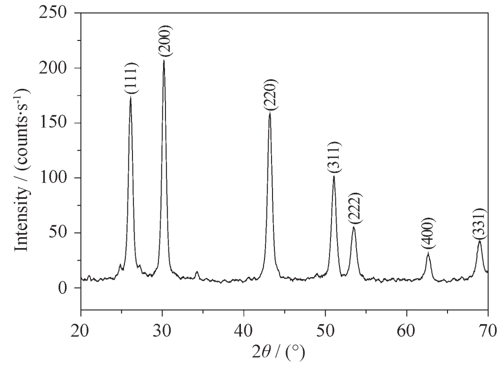

Fig.1 XRD pattern of PbS nanotubes

Fig.2 is the corresponding TEM photograph of PbS synthesized in bicontinuous microemulsion system. We can see that the as-prepared particles are in tubular shape. These nanotubes display a random distribution, smooth surface and fairly uniform diameter. The inner diameter of nanotubes is about 100 nm, the outer diameter is about 130 nm. The ends of these nanotubes are open.

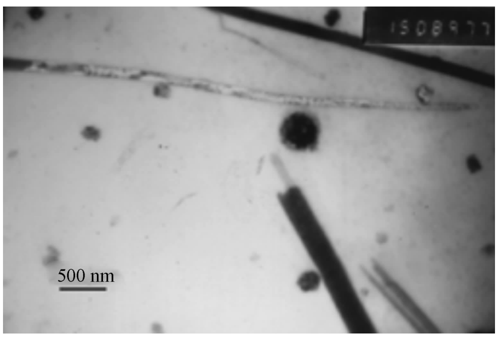

Fig.2 TEM images of PbS nanotubes

Formation of PbS nanotubes requires sufficient time. If the aging time is not enough, PbS can only grow into tiny particles absorbed on the inner wall of the water channels as proved by the TEM micrograph in Fig.2.

On the basis of the above results, we think that the formation of PbS nanotubes may be due to the tiny water channels in the bicontinuous microemulsion, which may provide a template for the nanoparticles growth. So, the formation mechanism of the PbS nanotubes is suggested as follows:

(1) Nucleation. After mixing the two microemulsion solutions containing Pb^{2+} and S^{2-} ions, the osmosis of Pb^{2+} and S^{2-} from one water channel to another occurs, and the nucleation of PbS from reaction of $Pb^{2+}+S^{2-}=PbS$ takes place rapidly.

(2) Growth. Once a nucleus forms, it will continue to grow into tiny nanoparticles by a continued deposition of Pb^{2+} and S^{2-} on the nuclei.

(3) Assemblage. The tiny PbS nanoparticles are absorbed onto the inner wall of the water channels, providing a tubular template for the tiny PbS nanoparticles to grow into nanotubes.

(4) Crystallization. The tiny PbS nanoparticles further assemble under the inducement of the tubular template, fuse, crystallize, thus shapes are tuned according to the template. Once the amalgamation and growth of nanoparticles reach to a certain degree, the nanotubes are formed.

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