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Solvothermal preparation of tin phosphide nanorods

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Abstract

Sn_4P_3 nanorods 20 × 400 nm were successfully synthesized through a solvothermal process based on a metathesis reaction between $SnCl_2$ and Na_3P at 120–140°C, using ethylenediamine as the solvent and template. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One-dimensional structures with nanometer diameters, such as nanorods and nanotubes, are currently the focus of much research due to their special properties [1]. Compared with micrometer-diameter whiskers, these fascinating systems are expected to exhibit remarkable mechanical properties, as well as electrical, optical, and magnetic properties, quite different from their corresponding bulk materials [2]. These new nanoscale materials have potential applications in both mesoscopic research and development of nano devices. Previous works in this field focused on carbon nanorods and nanotubes, which are the by-products of fullerene research [3]. Carbon nanorods or nanotubes are grown conventionally by arc discharge at a temperature of about 3000 K [4], thermal deposition of hydrocarbons [5], and vapor–liquid–solid (VSL) growth [6]. Comparatively little research has been conducted on other one-dimensional materials. Further, nearly all of the methods previously used to

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prepare nanorods or nanotubes need extreme conditions. How to prepare nanoscale materials under milder conditions is an important goal of materials chemists.

Preparation of metal phosphides is a pressing problem in science and engineering at present [7]. These materials are technologically important as semiconductors, luminescent devices, and electronic components. Metal phosphides are made conventionally by direct combination of elements or by the reaction of highly toxic phosphides with metal or metal hydride via the metal organic chemical vapor deposition or self-propagation high-temperature synthesis route. These procedures typically require high reaction temperatures (above 1000°C sometimes) and long annealing periods, to produce the crystalline materials [8–10]. For example, Sn_4P_3 can be obtained by heating stoichiometrical elements in sealed evacuated silica tubes at temperatures between 400 and 545°C [11]. Recently, Parkin [12] reported using a solid-state metathesis (SSM) reaction to prepare metal phosphides and arsenides, such as FeP and InAs, at high temperatures, but tin phosphide was not included. In this work, pure Sn_4P_3 nanorods were successfully synthesized through a solvothermal process based on a metathesis reaction between $SnCl_2$ and Na_3P at 120–140°C. Ethylenediamine was used as the solvent and the morphology template.

2. Experimental

Preparation included two steps:

1. The formation of Na_3P: An appropriate amount of analytically pure yellow phosphorus was washed free of water by using absolute ethanol and toluene respectively, and sodium was free of kerosene by using toluene. Both yellow phosphorus and sodium were used without further purification. Next they were put into a Teflon-lined autoclave of 100 ml capacity immediately after toluene was put into the autoclave up to 75% of the total volume. The autoclave was maintained at 150°C for 5 h, then cooled to room temperature naturally. A black precipitate of Na_3P was obtained.
2. The formation of Sn_4P_3: The solution of toluene was drawn off carefully, then an appropriate amount of $SnCl_2$ in ethylenediamine was added into the autoclave. The autoclave was filled with nonhydrous ethylenediamine up to 75% of the total volume, maintained at 120–140°C for 12 h, and then cooled to room temperature naturally. The gray precipitate obtained was collected and washed with benzene, absolute ethanol, and distilled water several times. The final product was dried in vacuum at 60°C for 2 h.

The samples were characterized by powder X-ray diffraction (XRD) patterns employing a scanning rate of $0.05° \ s^{-1}$ in 2θ range from 20° to 60°, using a Rigaku D/max γA X-ray diffractometer equipped with a graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å). The morphology of the products was determined by transmission electron microscopy (TEM), on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV. The purity and composition were studied by the X-ray photoelectron spectra (XPS) on an ESCALab MKII instrument, with Mg Kα radiation as the exciting source.

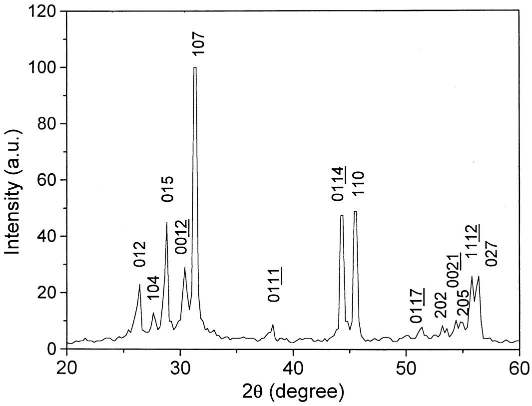

Fig. 1. XRD pattern of the as-prepared Sn_4P_3 nanorods.

3. Results and discussion

All peaks in the XRD pattern (Fig. 1) were indexed to the hexagonal cell of Sn_4P_3 with $a = 3.98$, $c = 35.34$ Å, in good agreement with JCPDS No. 20-1294. The TEM image (Fig. 2) indicated that the diameter of the nanorods was about 20 nm and the length was up to 400 nm. XPS results (Fig. 3) showed the mole ratio to be Sn:P = 1.44:1, which is close to the ratio in the form Sn_4P_3. From the XPS results, one can see that there was a little oxygen, due to absorption oxygen on the surface of nanocrystalline Sn_4P_3. In fact, the absorption of oxygen is very common to powder samples with high special surface area that have been exposed to atmosphere.

It is well known that the solvents affect grain morphology [13]. In our experiments, different solvents were tested and the results revealed that the kind of solvents used was the most influential factor on the quality of the Sn_4P_3 nanorods. Ethylenediamine was chosen due to its N-chelation and structure. It possibly binds to Sn(II), to produce a complex. The dissolution of $SnCl_2$ in ethylenediamine and formation of a complex increased the surface area of $SnCl_2$ and caused the reaction to occur in the solid–liquid system. The solvent

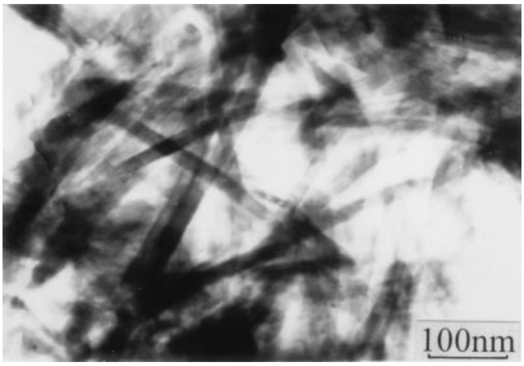

Fig. 2. TEM image of the as-prepared Sn_4P_3 nanorods.

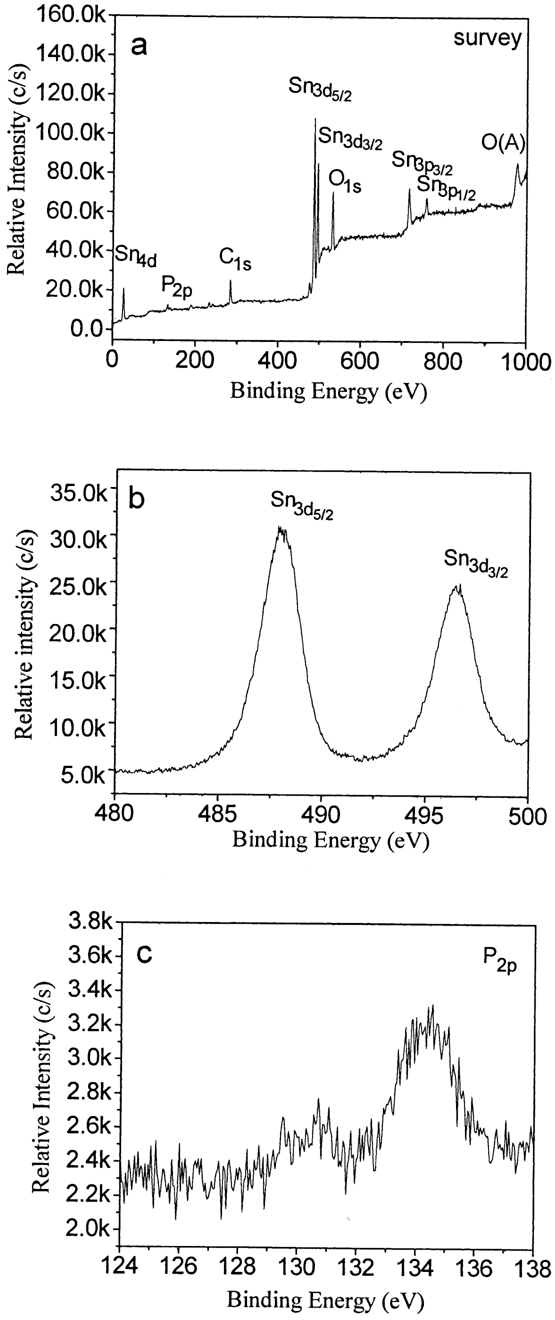

Fig. 3. XPS analyses of as-prepared Sn_4P_3 nanorods. (a) Survey; (b) Sn region; (c) P region.

ethylenediamine enhanced the reactivity of $SnCl_2$ and promoted the reaction between $SnCl_2$ and Na_3P, without high temperature, unlike in solid-state metathesis. Thus, this pathway differs greatly from the solid-state reaction. Ethylenediamine probably served as a template, just as it does in the formation of molecular sieves. It controlled the nucleation of Sn_4P_3 grains, made the Sn_4P_3 grains grow in one direction, and finally resulted in the Sn_4P_3 nanorods. This is somewhat like the nanorod growth mechanism of VLS [6]. When other solvents with no N-chelation, such as benzene and tetrahydrofunan, were used, instead of ethylenediamine, no Sn_4P_3 nanorods were obtained, the metathesis reaction was incomplete, and there were large amounts of unreacted $SnCl_2$ in the products. These results clearly demonstrate that the particular structure and property of ethylenediamine play an important role in the formation of Sn_4P_3 nanorods.

The preparation of Sn_4P_3 nanorods through the solvothermal process was found to be dependent on several other factors, including temperature, reaction time, and the valence state of tin salts. In the first solvothermal step, the optimum condition for the formation Na_3P was 150°C for 5 h. As an aromatic solvent was essential to preparing sodium phosphide in liquid phase [14], toluene was chosen because of its appropriate boiling point. It was observed that at least 20–30% excess yellow phosphorus in toluene was essential to ensure the complete conversion of Na to Na_3P. Some excess phosphorus could be involved in the subsequent reaction with $SnCl_2$. Excess phosphorus was dissolved in toluene and removed with the draw of toluene.

The optimum condition for synthesizing pure phase of Sn_4P_3 was 120–140°C for 12 h. As the temperature was lower than 100°C and the time was less than 8 h, the yield of the Sn_4P_3 was lower. A higher temperature than 140°C or longer time than 12 h, however, had no significant effect on the formation and quality of the products. The byproduct of NaCl, a small amount of excess P, or possibly unreacted Na_3P, could be removed by washing with benzene, absolute ethanol, and water. Experiments showed that the kind of tin salts was also a critical factor for the purity of products. When tin tetrachloride was used, the product was a mixture of Sn_4P_3, SnP, and a small amount of unknown materials; whereas, when tin dichloride was used, pure phase of Sn_4P_3 was obtained. The whole reaction can be expressed as follows:

$$12SnCl_2+8Na_3P + P \xrightarrow{ethylenediamine} 3Sn_4P_3 + 24NaCl$$

4. Conclusions

In summary, Sn_4P_3 nanorods were successfully obtained through a mild and simple solvothermal route. Reaction conditions including solvent, temperature, and the valence state of raw materials tin salts are important factors to the morphology, crystallization, and purity of nanocrystalline Sn_4P_3. Based on the results of the present study, we will synthesize other kinds of metal phosphide nanorods through this route, to determine its scope.

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