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A Novel One-Step Solvothermal Route to Nanocrystalline Sn_4P_3

H. L. Su,*,† Y. Xie,†,[1] B. Li,† X. M. Liu,* and Y. T. Qian*,†

**Structure Research Lab and †Department of Chemistry, University of Science & Technology of China, Hefei, Anhui 230026, P.R. China*

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A novel solvothermal method has been successfully developed to obtain nanocrystalline Sn_4P_3 in an autoclave based on the reaction of $SnCl_2 \cdot 2H_2O$ with yellow phosphorus at 160°C for 10 h, with potassium borohydride (KBH_4) used as the reducing agent and ethanol as the solvent. XRD, TEM, and XPS examinations investigated the phase, grain size, morphology, and purity of the product, respectively. The product is spherical nanocrystalline Sn_4P_3 with a hexagonal structure. Potassium borohydride and ethanol played important roles in the formation of nanocrystalline Sn_4P_3. A possible mechanism is proposed as: under the solvothermal condition, Sn^{2+} was steadily reduced by KBH_4 to atomic Sn; subsequently these newborn active atoms homogeneously combined with yellow phosphorus to form nanocrystalline Sn_4P_3. © 1999 Academic press

INTRODUCTION

Despite the tremendous interest in using transition metal carbides and nitrides as catalysts for the past decade (1), analogous phosphides have received less attention. In fact, many phosphides are excellent catalysts of some important reactions. For example, tin phosphide (Sn_4P_3) is an excellent catalyst of alkylation reactions (2–4). Furthermore, almost all transition metals and some main group elements can form phosphides, with the compositions ranging from M_3P to MP_3 (5–8). In addition, there are many ternary mixed-metal phosphides, such as phosphide nitrides, phosphide sulfides, and phosphide selenides. These flexible compositions afford a favorable opportunity of obtaining new catalysts.

Conventionally, there are several methods for metal phosphides (9, 10), such as (a) the direct reactions of elemental metal and phosphorus heated in vacuum or in an inert atmosphere, (b) the isothermal reduction of metal phosphates with carbon or hydrogen at high temperature, (c) the co-heating of metal elements or metal halides and the phosphines, and (d) the electrolysis of molten salts containing the metal oxides and alkali phosphates at high temperature. However, these preparation methods usually require very high temperature (>1000 K) (11–13), resulting in sintered materials with high crystallinity and large grain sizes. Furthermore, studies have revealed that the catalysis will be limited as the specific surface area of the material decreases (11, 14). In addition, the use of toxic phosphine compounds also raises environmental problem (14). So it is urgent for materials scientists to look for mild and safe routes to nanocrystalline metal phosphides with larger specific surface area.

The solvothermal pathway is a newly developing effective method to prepare nanocrystalline materials, which does not require organometallic or toxic precursors and is carried out under mild conditions. The organic solvent plays an important role in controlling the nucleation and growth of nanocrystalline materials. Compared with other methods, the solvothermal route is convenient, simple, mild, and easy to control. With suitable organic solvents, some new reactions can be carried out and the morphologies and properties of the materials can also be controlled. We have obtained many nanocrystalline nonoxides based on different solvothermal reactions under mild conditions (15–18). On the other hand, among various organic slovents, ethanol is nontoxic and the cheapest and most convenient. Furthermore, with suitable temperature and pressure, $SnCl_2 \cdot 2H_2O$ and KBH_4 are soluble in the ethanol so that Sn^{2+} is easily reduced by KBH_4. In this work, we report our current progresses in the synthesis of metal phosphides. A novel one-step solvothermal route was developed to obtain hexagonal phase nanocrystalline Sn_4P_3 with ethanol used as the solvent and KBH_4 as the reducing agent.

EXPERIMENTAL

The solvothermal processes were carried out in a Teflon-lined stainless steel autoclave. Analytically pure $SnCl_2 \cdot 2H_2O$ (2.256 g, 10 mmol), yellow phosphorous (0.240 g, 7.74 mmol), and KBH_4 (0.540 g, 10 mmol) were added into an autoclave, which had been filled with absolute ethanol up to 90% of its capacity (100 ml). The autoclave was kept at 160°C for 10 h, then cooled to room temperature naturally.

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[1] To whom correspondence should be addressed.

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The precipitate was filtered, washed with distilled water, and dried in vacuum at 70°C for 4 h. The final white product was collected for characterizations.

The phase and grain sizes of the product were known by the X-ray powder diffraction (XRD) patterns, which were performed with a Japan Rigaku D/max-γA rotation anode X-ray diffractometer using monochromatic high-intensity Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The morphology and size were determined by the Hitachi H-800 transmission electron microscope (TEM), with the 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$K\alpha$ radiation as the exciting source.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the prepared nanocrystalline Sn_4P_3. All the peaks could be indexed to single hexagonal phase of Sn_4P_3. The cell constants were calculated to be $a = 3.9701$ Å and $c = 35.012$ Å, which are close to the reported values $a = 3.9677$ Å and $c = 35.331$ Å (19). The mean crystalline size is 20 nm, as calculated from the half-width of the diffraction peaks using Scherrer's equation (20). From the TEM image as shown in Fig. 2, it is obvious that the nanocrystalline Sn_4P_3 particles are nearly spherical, but are not homogeneous. Some are less than 20 nm, and other larger particles are the aggregations of small ones, indicating that the small particles of nanocrystalline Sn_4P_3 easily aggregate into secondary particles due to their extremely small dimension and high surface energy. XPS results also showed the mole ratio as Sn:P = 1.44:1, which is close to the ratio in the form Sn_4P_3. And from XPS, one can see that there is 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 which have been exposed to atmosphere.

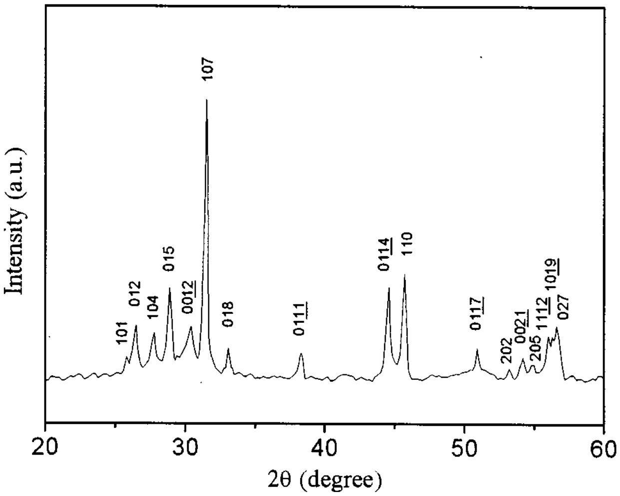

FIG. 1. XRD patterns of as-prepared nanocrystalline Sn_4P_3.

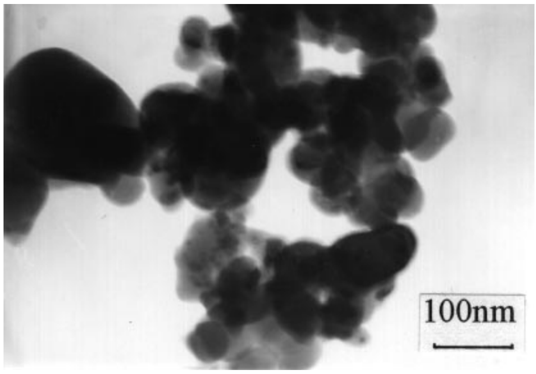

FIG. 2. TEM image of as-prepared nanocrystalline Sn_4P_3.

Here, potassium borohydride and ethanol were an important reducing agent and solvent, respectively. Under the solvothermal conditions, it was tested that KBH_4 was soluble in ethanol. Furthermore, ethanol and water are always mutually soluble. So under the solvothermal conditions, KBH_4 and $SnCl_2 \cdot 2H_2O$ could dissolve together in the mutually soluble solvents of ethanol and trace water. Thus Sn^{2+} and KBH_4 were homogeneously dispersed in the system and Sn^{2+} would be easily reduced by the KBH_4 to active atomic Sn. Subsequently, these active atoms would easily react with active yellow phosphorus to form Sn_4P_3. The whole process can be described by the following reactions:

$$Sn^{2+} \xrightarrow{KBH_4} Sn$$

$$16Sn + 3P_4 \rightarrow 4Sn_4P_3.$$

When KBH_4 reduced Sn^{2+} to atomic Sn, large amounts of gas would rapidly evolve. However, in the sealed autoclave and at certain temperature, the generation of the gases and the reduction process would be limited. Thus the tin atoms would steadily yield and the nucleation and growth of nanocrystalline Sn_4P_3 could be controlled.

On the other hand, similar reactions could not be initiated under the same solvothermal conditions if the starting material $SnCl_2 \cdot 2H_2O$ was substituted by elemental tin or without reducing agent KBH_4. In addition, when $SnCl_2 \cdot 2H_2O$ and KBH_4 were added into an open vessel, a black precipitation appeared and tested as elemental tin by the XRD analysis. Subsequently, yellow phosphorus was added into the system, no new reactions continued, and no tin phosphides could be obtained even if following a similar solvothermal process, indicating that comparing with newborn atomic tin, the precipitated elemental tin had lost its activity. On the other hand, other tin phosphides, such as

SnP, SnP_3, were never detected in the products by XRD and XPS, indicating that under the solvothermal conditions, Sn_4P_3 might be the most stable one and be easiest to form among all the tin phosphides. From above, one can see that only newborn tin atoms were active enough to combine with active yellow phosphorus to form Sn_4P_3, and Sn_4P_3 was easiest to form in many tin phosphides.

In this work, suitable temperature and reaction time not only brought out the whole reactions, but also controlled the purity, crystallinity, and size of the product. Optimum conditions for preparing nanocrystalline Sn_4P_3 were at 160°C for 10 h. Lower temperature ($\leq$140°C) or shorter time led to incomplete reactions which decreased the yield and crystallinity, with elemental tin appearing in the product Sn_4P_3. On the other hand, at higher temperature or for a longer time, the resultant crystalline grains grew larger and it was difficult to obtain nanocrystals. So only at suitable temperature, when newborn tin atoms were active enough and phosphatization reactions could be initiated, the nucleation and growth of crystalline Sn_4P_3 could be controlled, pure nanocrystalline Sn_4P_3 could be obtained.

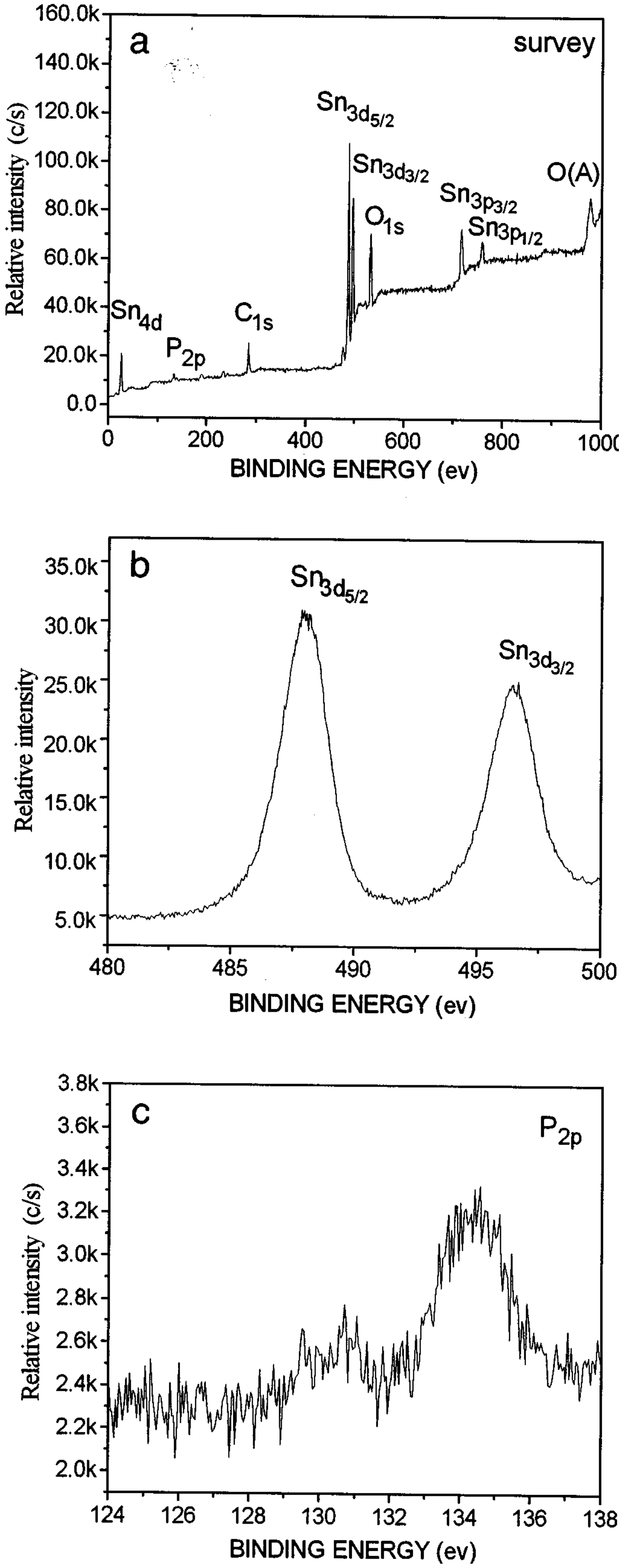

FIG. 3. XPS analyses of as-prepared nanocrystalline Sn_4P_3.

CONCLUSIONS

In summary, spherical nanocrystalline Sn_4P_3 with a hexagonal structure was successfully obtained through a mild solvothermal process at 160°C for 10 h, based on the reaction of $SnCl_2 \cdot 2H_2O$ with yellow phosphorus in an ethanol system with KBH_4 used as the reducing agent. In this process, reducing agent KBH_4, solvent ethanol, starting materials, reaction temperature, and time were important factors in the formation of nanocrystalline Sn_4P_3.

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