Microwave synthesis of nanocrystalline metal sulfides in formaldehyde solution

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Abstract

Nanocrystalline metal (Cu, Hg, Zn, Bi, Pb) sulfides with different shapes and different particle sizes have been successfully prepared in a formaldehyde solution of metal salt and thioacetamide by microwave irradiation. Powder X-ray diffraction patterns indicated that the products were pure orthorhombic Bi₂S₃ phase, cubic phase HgS, hexagonal phase CuS, cubic phase ZnS, cubic phase PbS, respectively. The products were also characterized by transmission electron microscopy. Ultraviolet reflection spectrum clearly indicates the presence of quantum size effects in ZnS. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, nanoparticles have been investigated intensively because of their size-dependent properties and the possibility of arranging them in micro (and nano) assemblies [1–5]. Intriguing prospects for the development of novel electronic devices, electrooptical applications, and catalysis have also been suggested [6–8].

Semiconductor nanoparticles, in particular, exhibit variable and controllable properties, especially, the change of energy structure and enhanced surface properties with a decrease in size that affects their optoelectronic properties. They have been prepared from many different semiconductors in different forms, such as colloids, powder, and deposits on substrates, and by a variety of methods [9].

Metal sulfides show novel optical and electrical properties, and some of them are used for the fabrication of devices. A variety of methods can be used to prepare the semiconductor metal sulfide nanoparticles, such as direct element reaction in a quartz vessel at high temperature [10,11], ball mill solid-state metathesis reaction [12], the chemical deposition method [13], thermal decomposition method [14], hydrothermal method [15], solvothermal method [16], sonochemical method [17], electrochemical method [18]. Some reactions require high temperature for initiating the reaction, using toxic H₂S as source or the final products containing some impurities.

Obtaining materials under simpler conditions have been a goal of many scientists. Traditional methods usually need high temperature, and/or high pressure, and/or inert atmosphere protection, and/or toxic organometallic precursors and it is difficult to grow nanocrystalline materials under such conditions. However, nanoscale materials are becoming important for studying the variation of a material’s property with size.

Since 1986, microwave irradiation as a heating method has found a number of applications in chemistry. The microwave synthesis, which is generally quite fast, simple, and energy efficient, has been developed, and widely used for zeolites and ceramic materials, etc.

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[19–27]. Compared with conventional method, microwave synthesis has the advantages of very short time, small particle size, narrow particle size distribution, and high purity. Jansen et al. suggested that these advantages could be attributed to fast homogeneous nucleation and the easy dissolution of the gel [19]. Unfortunately the exact nature of the interaction of the microwaves with the reactants during the synthesis of materials is somewhat unclear and speculative. However, it is well known that the interaction of dielectric materials, liquids or solids, with microwaves leads to what is generally known as dielectric heating. Electric dipoles present in such materials respond to the applied electric field. In liquids, this constant reorientation leads to friction between molecules, which subsequently generates heat [27].

In this study, we report on the preparation of metal (Cu, Hg, Zn, Bi, Pb) sulfide nanoparticles in a formaldehyde solution of metal salt and thioacetamide (TAA) by microwave irradiation. The products were characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD).

2. Experimental

2.1. Materials

The starting materials for the synthesis of metal (Cu, Hg, Zn, Bi, Pb) sulfide powders were Bi(NO$_3$)$_3$·5H$_2$O, Zn(CH$_3$COO)$_2$·2H$_2$O, Cu(CH$_3$COO)$_2$·H$_2$O, Hg(CH$_3$COO)$_2$, Pb(CH$_3$COO)$_2$·3H$_2$O, and TAA. All the chemicals are used as received. Distilled water was used throughout the experiments.

![Image of TEM images](image_url)
2.2. Instruments

Microwave oven with 650 W (Sanle general electric corp. Nanjing, China) with refluxing system was used. Powder XRD patterns were recorded on Shimadzu XD-3A X-ray diffractometer (Cu Kα radiation, λ = 0.15418 nm). Transmission electron micrographs were obtained with a JEOL-JEM 200CX electron microscope (TEM), using an accelerating voltage of 200 kV. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon.

2.3. Synthesis of nanocrystalline metal sulfides

In a typical procedure, an appropriate amount of metal salt was dissolved in 100 ml formaldehyde. Then, an appropriate amount of TAA was added into the solution. Finally, a flask of 250 ml was filled with the mixture solution. The mixture solution was reacted in a microwave refluxing system for 20 min with power 20% (The means of 20% power is that microwave operates in 30 s cycle, on for 6 s, off for 24 s. The total power is still 650 W). After cooling to room temperature naturally, the precipitate was centrifuged, washed with distilled water, and dried in the air. The final products were collected for characterizations.

3. Results and discussion

Fig. 1 shows electron micrographs of as-prepared metal sulfides. The products of HgS grains are spherical with 8–12 nm particle size in Fig. 1a. The products of CuS grains also are found to be spherical with 5–10 nm particle size in Fig. 1b. Fig. 1c is apparent that as prepared Bi₂S₃ is nanorods with a diameter of 50 nm and a length of up to 2 μm. Fig. 1d shows that the ZnS is spherical with ≈ 3 nm particle size. However, some aggregation is observed in this figure, which is believed to arise from agglomeration at the drying stage owing to the large surface energy of the particles. Fig. 1e shows the as-prepared PbS, which is sheet-type.

The XRD patterns of the as-prepared products are shown in Fig. 2. The diffraction peaks in the patterns in Fig. 2a–e correspond to the reflections of cubic phase ZnS (JCPDS File No. 5-0566), hexagonal phase CuS with 8–12 nm particle size in Fig. 1a.
(JCPDS File No. 6-0464), cubic phase HgS (JCPDS File No. 6-0261), orthorhombic phase Bi$_2$S$_3$ (JCPDS File No. 17-320), cubic phase PbS (JCPDS File No. 5-0592), respectively. The grain sizes of HgS, CuS and ZnS samples as calculated from the half-width of the diffraction peaks using the Debye–Scherrer equation, are ≈ 10, 7 and 3 nm, respectively. These results are in good agreement with TEM results.

Fig. 3 shows the ultraviolet diffusion reflection spectrum of as-prepared ZnS. It exhibits the optical reflection edge at ≈ 300 nm. The absorption edges of ZnS are blue-shifted from the absorption edge of bulk ZnS. According to the spectrum, we estimate the bandgap of ZnS to be 4.13 eV (bulk ZnS 340 nm, 3.65 eV [28,29]). This value corresponds to that reported for the 3 nm ZnS particles [26]. This clearly indicates the presence of quantum size effects in the prepared ZnS by microwave irradiation.

The effects of microwave power, reaction time and reactant quantity ratio on the formation of crystalline metal sulfides were investigated. Microwave power and reaction time have influence on the formation of crystalline metal sulfides. The effects of experiment show that bumping would occur and the yields were low when the power was larger than 40%. The reason is that H$_2$S, decomposing from TAA on overheating, is easy to evaporate. When the reaction time was less than 10 min the crystalline products were not formed. The ratios of metal salt to TAA were 1:1.2, except for Bi$^{3+}$ to TAA, which was 2:3.5.

We explain this phenomenon of producing nanocrystalline metal (Cu, Hg, Bi, Zn, Pb) sulfides due to the high rate of the reactions resulted from the microwave irradiation, which provides higher energy. We also found that the size and the shape of CuS, HgS, Bi$_2$S$_3$, ZnS, and PbS were different in the same microwave irradiation time. It showed that microwave irradiation could influence selective nucleation and growth rates of different compounds. The reactions occurring during microwave irradiation which lead to nanocrystalline metal (Cu, Hg, Bi, Zn, Pb) sulfides are believed to be [26]:

\[
\begin{align*}
\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} & \rightarrow \text{CH}_3(\text{NH}_2)\text{C(OH)}\text{–SH} \quad (1) \\
\text{CH}_3(\text{NH}_2)\text{C(OH)}\text{–SH} + \text{H}_2\text{O} & \rightarrow \text{CH}_3(\text{NH}_2)\text{C(OH)}_2 + \text{H}_2\text{S} \quad (2) \\
\text{CH}_3(\text{NH}_2)\text{C(OH)}_2 + \text{H}_2\text{S} & \rightarrow \text{CH}_3(\text{NH}_2)\text{C–O} + \text{H}_2\text{O} \quad (3) \\
\text{H}_2\text{S} + \text{M(CH}_3\text{COO})_2 & \rightarrow \text{MS} + 2\text{CH}_3\text{COOH} \quad (4) \\
3\text{H}_2\text{S} + 2\text{Bi(NO}_3)_3 & \rightarrow \text{Bi}_2\text{S}_3 + 6\text{HNO}_3 \quad (5)
\end{align*}
\]

Eq. (1) represents that the H$_2$O reacts with CH$_3$CSNH$_2$ to form CH$_3$(NH$_2$)C(OH)-SH by microwave heating. Repeating this process would then result in formation CH$_3$(NH$_2$)C(OH)$_2$ and H$_2$S, CH$_3$(NH$_2$)C(OH)$_2$ would immediately lose water to give CH$_3$CONH$_2$, Eq. (3) shows the results. Then further H$_2$S reacts with M(Ac)$_2$ or Bi(NO$_3$)$_3$ to yield nanocrystalline MS and Bi$_2$S$_3$, Eqs. (4) and (5) show the results.

4. Conclusion

Nanocrystalline metal (Cu, Hg, Bi, Zn, Pb) sulfides have been prepared by the microwave method. The advantages of this process are that it is a simple, fast and efficient for producing nanocrystalline metal sulfides. We can foresee the upscaling of the process to form large quantities of this kind of nanomaterials.

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References


