Microwave-Assisted Synthesis of Sulfide M_2S_3 (M = Bi, Sb) Nanorods Using an Ionic Liquid

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Single-crystalline Bi_2S_3 and Sb_2S_3 nanorods have been successfully synthesized by the microwave-assisted ionic liquid method. The starting reagents were Bi_2O_3 or Sb_2O_3, HCl, $Na_2S_2O_3$, and ethylene glycol (EG) or ethanolamine, and the ionic liquid used was 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]). Our experiments showed that the ionic liquid played an important role in the morphology of M_2S_3 (M = Bi, Sb). Single-crystalline Bi_2S_3 nanorods could be prepared in the presence of [BMIM][BF_4]. However, urchinlike Bi_2S_3 structures consisting of nanorods were formed without using [BMIM][BF_4]. Single-crystalline Sb_2S_3 nanorods were obtained in the presence of [BMIM][BF_4]. However, single-crystalline Sb_2S_3 nanosheets could be prepared in the absence of [BMIM][BF_4]. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and electron diffraction (ED).

Introduction

Room-temperature ionic liquids (RTILs) have aroused increasing interest worldwide due to their high fluidity, low melting temperature, extended liquid-state temperature range, high ionic conductivity, ability to dissolve a variety of materials, and, importantly, lack of measurable vapor pressure.[1−4] RTILs offer possibilities for fundamental studies of their effects on chemical reactions and synthetic processes.[1−3,5] The advantages of RTILs for materials chemistry and especially for the synthesis of novel nanostructures have been recently realized.[6] There have been recent reports on the formation and stabilization using RTILs of TiO_2,[7−9] nanoparticles of Pd,[10] Ir,[11−13] Pt,[14,15] Rh,[12,16] Au,[15] Ag,[17] Ni,[18] and Al, Fe, Al−Mn alloy,[19] and Si.[20] These nanoparticles prepared in ionic liquids were spherical in shape, instead of being nanorods and nanowires. The application of microwave heating in synthetic chemistry is a fast-growing research area[21−24] due to its advantages such as rapid volumetric heating, higher reaction rate, and selectivity, reducing reaction time often by orders of magnitude and increasing yields of products compared to conventional heating methods. As a result, this has opened up the possibility of realizing fast synthesis of materials in a short time. From the perspective of microwave chemistry, one of the key important advantages of RTILs is the presence of large organic positive ions with a high polarizability. Therefore, RTILs are good media for absorbing microwaves, leading to a high heating rate. Recently, by combining the advantages of both RTILs and microwave heating, we have developed a new microwave-assisted ionic liquid method for fast controlled synthesis of nanorods and nanowires of Te[25] and ZnO.[26] Herein, we report for the first time that nanorods of metal sulfides M_2S_3 (M = Bi, Sb) can be synthesized by the microwave-assisted ionic liquid method. We demonstrate that the ionic liquid has a significant influence on the morphology of M_2S_3 (M = Bi, Sb).

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Experimental Section

All chemicals were purchased and used without further purification. The ionic liquid used was 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) (Fluka, Germany). In a typical procedure for synthesizing Bi_2S_3, Bi_2O_3 was dissolved in a mixture of ethylene glycol (EG) and 37 wt % hydrochloric acid aqueous solution in a 10-mL tube at room temperature (solution A). Solution B was prepared by dissolving $Na_2S_2O_3\cdot 5H_2O$ in [BMIM][BF_4]. Solution A was microwave-heated to 190 °C, and solution B was fast added into solution A. The mixed solution was maintained at 190 °C for 30 s or 10 min without stirring. Then microwave heating was terminated and the solution was cooled to room temperature. In other experiments, [BMIM][BF_4] was not used and $Na_2S_2O_3\cdot 5H_2O$ was dissolved in EG. The same procedure was used for the synthesis of Sb_2S_3 except that ethanolamine was used instead of EG, Sb_2O_3 was used instead of Bi_2O_3, and the temperature was 165 °C. The black products were separated by centrifugation, washed with absolute ethanol three times, and dried. The experimental conditions for some typical samples are listed in Table 1.

The microwave oven used for sample preparation was a focused single-mode microwave synthesis system (Discover, CEM, USA). The temperature was controlled by automatic adjusting of microwave power. X-ray powder diffraction (XRD) was performed with a Rigaku D/max 2550V X-ray diffractometer using graphite monochromatized high-intensity Cu Kα radiation (λ = 1.54178 Å). The transmission electron microscopic (TEM) micrographs and the electron diffraction (ED) patterns were taken with a Hitachi H-800 electron microscope with an accelerating voltage of 200 kV. The optical microscopic images were taken with a BM-12 optical microscope (Shanghai Optical Instruments Factory).

Results and Discussion

Figure 1 shows X-ray powder diffraction (XRD) patterns of two typical samples synthesized by the microwave-assisted ionic liquid method. Figure 1a shows that sample 2 consisted of a

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TABLE 1: Typical Samples Synthesized by the Microwave-Assisted Ionic Liquid Method

sample no.	reaction system	heating method	*T* (°C)	time	morphology
1	Bi_2O_3 (0.023 g) + ethylene glycol (EG) (1.5 mL) + 37 wt % HCl (0.08 mL) + $Na_2S_2O_3$ (0.036 g) + EG (0.5 mL)	microwave	190	10 min	urchinlike
2	Bi_2O_3 (0.023 g) + EG (1.5 mL) + 37 wt % HCl (0.08 mL) + $Na_2S_2O_3$ (0.036 g) + [BMIM][BF_4] (0.5 mL)	microwave	190	10 min	nanorods
3	Bi_2O_3 (0.023 g) + EG (1.5 mL) + 37 wt % HCl (0.08 mL) + $Na_2S_2O_3$ (0.036 g) + [BMIM][BF_4] (0.5 mL)	microwave	190	30 s	nanorods
4	Sb_2O_3 (0.011 g) + ethanolamine (1.8 mL) + 37 wt % HCl (0.08 mL) + $Na_2S_2O_3$ (0.028 g) + ethanolamine (0.2 mL)	microwave	165	60 min	nanosheets
5	Sb_2O_3 (0.011 g) + ethanolamine (1.8 mL) + 37 wt % HCl (0.08 mL) + $Na_2S_2O_3$ (0.028 g) + [BMIM][BF_4] (0.2 mL)	microwave	165	40 min	nanorods

single phase of crystalline Bi_2S_3 with orthorhombic structure (JCPDS 84-0279). Figure 1b shows that sample 5 was a single phase of crystalline Sb_2S_3 with orthorhombic structure (JCPDS 75-1310). Our experiments showed that other samples synthesized under different conditions (Table 1) were composed of a single phase of orthorhombic Bi_2S_3 or Sb_2S_3.

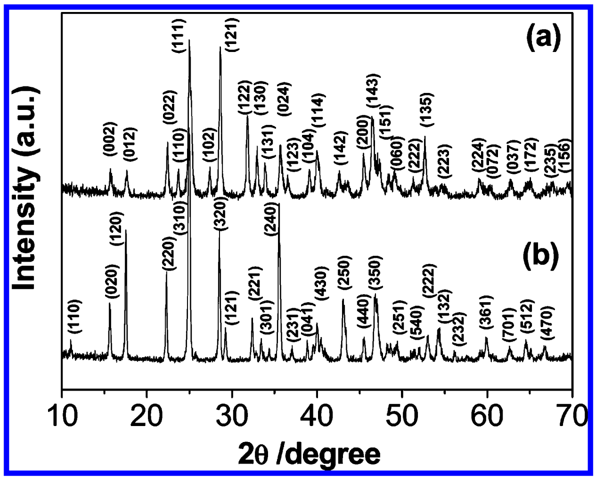

Figure 1. XRD patterns of two typical samples synthesized by microwave-assisted ionic liquid method: (a) sample 2 and (b) sample 5.

The morphologies of the samples were investigated by transmission electron microscopy (TEM). Figure 2a,b shows TEM micrographs of sample 1 (Bi_2S_3) synthesized under microwave heating at 190 °C for 10 min without using the ionic liquid [BMIM][BF_4], from which one can see the urchinlike morphology of Bi_2S_3. Each urchinlike structure consisted of a number of nanorods with diameters ranging from 50 to 100 nm and with lengths ranging from 300 to 600 nm. In a few cases, individual nanorods could be observed. The electron diffraction pattern of an individual nanorod (Figure 2c) indicates the single-crystalline structure of the nanorod. Tang and Qian et al.[27] reported a similar morphology of Bi_2S_3 prepared using $Bi(NO_3)_3$ and thiourea in ethylene glycol by conventional heating at 197 °C for 30 min. They also tried several other sulfur sources for the synthesis of urchinlike Bi_2S_3 structures but were not successful.

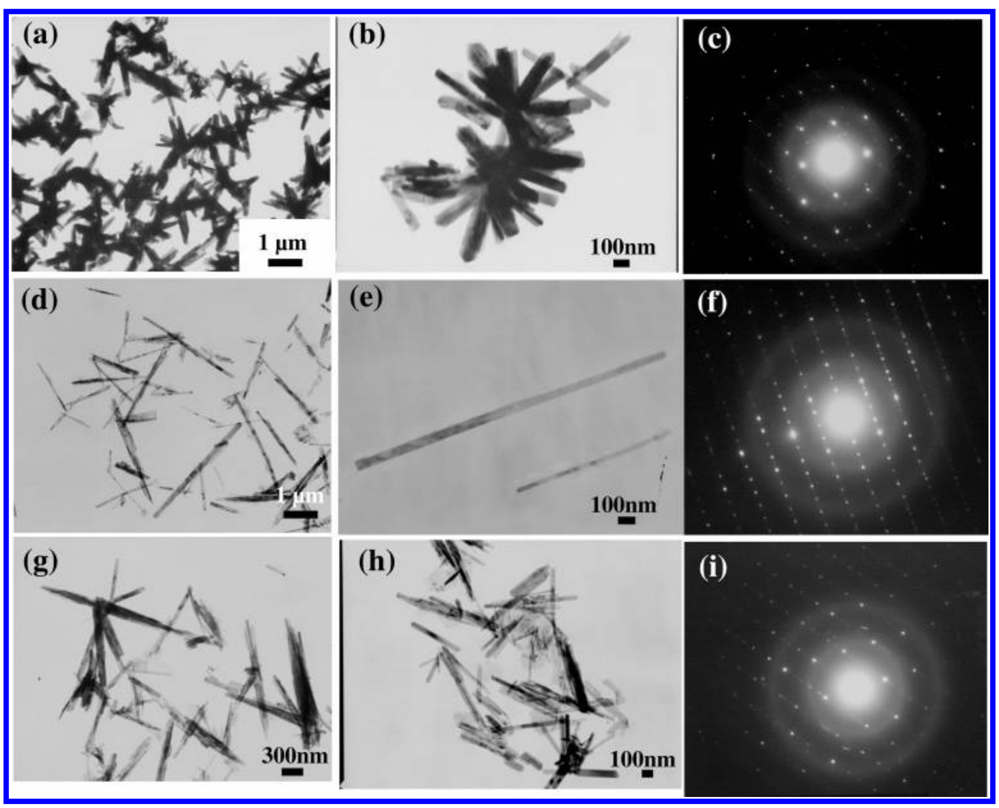

Figure 2. TEM micrographs of three typical Bi_2S_3 samples: (a and b) sample 1; (d and e) sample 2 synthesized via microwave-assisted ionic liquid method at 190 °C for 10 min; (g and h) sample 3 synthesized via microwave-assisted ionic liquid method at 190 °C for 30 s. (c, f, and i) Electron diffraction patterns of individual nanorods from samples 1, 2, and 3, respectively.

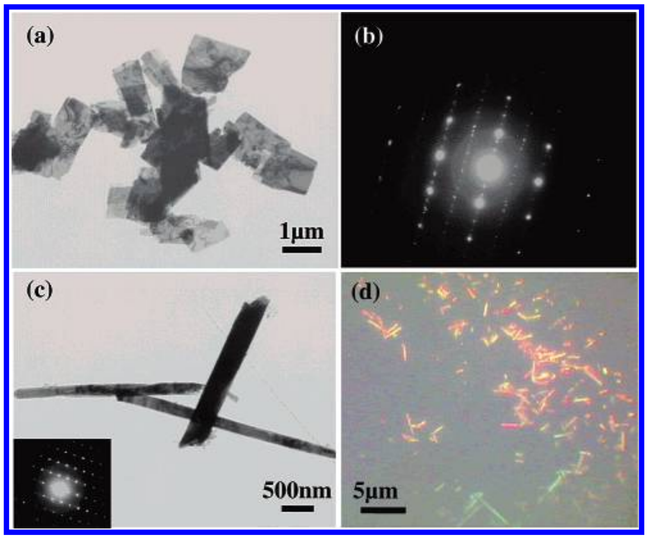

Figure 3. (a−c) TEM micrographs of two typical samples. (a) Sample 4. (b) Electron diffraction pattern of an individual nanosheet. (c) Sample 5; the inset shows the electron diffraction pattern of an individual nanorod. (d) Optical microscopic image of sample 5.

Figure 2d,e shows the morphology of sample 2 synthesized via the microwave-assisted ionic liquid method, from which one can see Bi_2S_3 nanorods with diameters less than 80 nm and with lengths up to several micrometers. Each nanorod is straight and has a uniform diameter along its entire length. The electron diffraction pattern of an individual nanorod shown in Figure 2f shows that it is single-crystalline. By comparing morphologies of samples 1 and 2, one can see the influence of [BMIM][BF_4] on the morphology of Bi_2S_3. In the presence of [BMIM][BF_4], longer and thinner Bi_2S_3 nanorods were prepared. In contrast, urchinlike Bi_2S_3 structures were formed in the absence of [BMIM][BF_4]. [BMIM][BF_4] may act as a surfactant in the formation of Bi_2S_3 nanorods. The role of the ionic liquid as a surfactant was also reported in the formation of Te nanorods and nanowires.[25]

Figure 2g,h shows TEM micrographs of sample 3 prepared under the same conditions as sample 2 except with microwave heating for 30 s instead of 10 min. The product consisted of single-crystalline Bi_2S_3 nanorods with diameters less than 60 nm and with lengths of several hundred nanometers. This demonstrates that fast synthesis of Bi_2S_3 nanorods can be realized in a short period of time (30 s) by the microwave-assisted ionic liquid method. In contrast, Bi_2S_3 nanorods could not be obtained by the conventional heating at 190 °C for 24 h.

The temperature has a significant influence on the formation of Bi_2S_3. Our experiments showed Bi_2S_3 could not be obtained at temperatures below 160 °C by microwave heating for 10 min.

The microwave-assisted ionic liquid method can also be extended to the synthesis of other sulfides, for example, Sb_2S_3. Figure 3a shows a TEM micrograph of Sb_2S_3 (sample 4) prepared in the absence of [BMIM][BF_4], from which one can see irregularly shaped Sb_2S_3 nanosheets with lateral sizes in the range of 500 nm−1.5 μm. These Sb_2S_3 nanosheets were single-crystalline in structure (Figure 3b). Sb_2S_3 has a layered orthorhombic structure that is favorable for the formation of sheetlike morphology. To our knowledge, there has been no report on the synthesis of Sb_2S_3 nanosheets. It is interesting that Sb_2S_3 nanorods were formed in the presence of [BMIM]-[BF_4] (sample 5). Figure 3c shows a TEM micrograph of Sb_2S_3 (sample 5), from which one can see single-crystalline Sb_2S_3 nanorods with lengths up to $\approx$3 μm and diameters of $\approx$200 nm. The inset of Figure 3c shows the electron diffraction pattern of an individual nanorod. The optical microscopic image (Figure 3d) shows a low-magnification image of Sb_2S_3 rods. These results demonstrate the significant effect of the ionic liquid on the morphology of the sulfides prepared.

More time was needed for synthesis of Sb_2S_3 when conventional heating was used instead of microwave heating. No black Sb_2S_3 could be obtained using conventional heating at 165 °C for 6 h. In contrast, Sb_2S_3 could be obtained by microwave heating at 165 °C for a relatively short period of time (40 min). When [BMIM][BF_4] was not used, no black Sb_2S_3 could be obtained by microwave heating for 40 min.

We propose the following chemical reactions involved in the formation of sulfides:

$$M_2O_3 + H^+ \rightarrow M^{3+} + H_2O \qquad (M = Bi, Sb)$$

$$M^{3+} + S_2O_3^{\ 2-} + H^+ \rightarrow M_2S_3 + H_2O + SO_2$$

The detailed formation mechanisms of Bi_2S_3 and Sb_2S_3 nanorods under microwave heating need to be further investigated.

Conclusion

The microwave-assisted ionic liquid method has been successfully used for fast synthesis of single-crystalline M_2S_3 (M = Bi, Sb) nanorods without using any surfactant, seed, or template. The ionic liquid plays an important role in the morphology of M_2S_3 (M = Bi, Sb). In the presence of [BMIM]-[BF_4], longer and thinner Bi_2S_3 nanorods were prepared. In contrast, urchinlike Bi_2S_3 structures consisting of nanorods were formed in the absence of [BMIM][BF_4]. Irregularly shaped single-crystalline Sb_2S_3 nanosheets could be prepared in the absence of [BMIM][BF_4]. However, single-crystalline Sb_2S_3 nanorods were formed in the presence of [BMIM][BF_4]. We expect that the microwave-assisted ionic liquid method may also be extended to fast synthesis of nanostructures of other metal sulfides. Related studies are in progress.

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