Microwave-assisted Synthesis of Nanocrystalline Metal Sulfides Using an Ionic Liquid

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Nanoparticles of metal sulfides (ZnS and CdS) have been successfully synthesized using an ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) under microwave heating at 100 °C for 10 min. The products were characterized by X-ray powder diffraction (XRD) and transmission electron microscopy (TEM).

Room-temperature ionic liquids (RTILs) have aroused increasing interest worldwide due to their high fluidity, low melting temperature and extended temperature range of liquid-state, air- and water-stability, low toxicity, non-flammability, high ionic conductivity, ability to dissolve a variety of materials and importantly no measurable vapor pressure.[1–4] Therefore, negative environmental and safety problems arising through the use of volatile organic solvents can be avoided by using RTILs. RTILs are actively being explored as possible "green" solvents[5] to substitute conventional volatile organic solvents. They also offer possibilities for fundamental studies of their effects on chemical reactions and synthetic processes.[1–3,6] There have been a few reports on the formation and stabilization using RTILs of hollow TiO_2 microspheres,[7] and nanoparticles of Pd,[8] Ir,[9] Pt,[10,12] Ag,[11] Au,[12] and polyaniline,[13] etc. Electrochemical deposition of nanocrystalline metals such as Al, Fe, and Al–Mn alloy has also been reported.[14]

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 very good media for absorbing microwave, leading to a very high heating rate. Recently, by combining advantages of both RTILs and microwave heating, we have developed a new microwave-assisted ionic liquid (MAIL) method for fast controlled synthesis of tellurium (Te) nanorods and nanowires.[15] Here, we demonstrate that the MAIL method can be successfully extended to synthesize nanoparticles of metal sulfides (ZnS and CdS). To our knowledge, there has been no report on the synthesis of nanocrystalline metal sulfides by using an ionic liquid under microwave heating.

All chemicals used were of analytical grade and used as received without further purification. Sample 1 was prepared as follows: $Zn(CH_3COO)_2{\cdot}2H_2O$ (40 mg) was dissolved in an ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) (0.5 mL) in a 10-mL tube by magnetic stirring at room temperature. The solution was microwave-heated to 100 °C, and 0.5-mL $Na_2S{\cdot}9H_2O$ aqueous solution (30 mg $Na_2S{\cdot}9H_2O$) was added immediately. The solution was maintained at 100 °C for 10 min, then microwave heating was terminated and the solution was cooled to room temperature. Sample 2 was prepared as follows: $CdCl_2{\cdot}2.5H_2O$ (15 mg) was dissolved in [BMIM]BF_4 (0.5 mL) by a magnetic stirrer in a 10 mL tube at room temperature. The solution was microwave-heated to 100 °C, and 0.5 mL $Na_2S{\cdot}9H_2O$ aqueous solution (50 mg $Na_2S{\cdot}9H_2O$) was added immediately. The solution was maintained at 100 °C for 10 min, then microwave heating was terminated and the solution was cooled to room temperature. The products were separated by centrifugation, washed with ethanol two times and deionized water two times, and dried at 60 °C. The microwave oven used for sample preparation was a focused single-mode microwave synthesis system (Discover, CEM, USA). The unique, circular single-mode cavity focuses the microwave on the reactants, ensuring the sample was in a homogenous highly dense microwave field. The system was equipped with a magnetic stirrer and a water-cooled condenser. Temperature was accurately 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 ($\lambda = 1.54178$ Å). The XRD patterns of samples 1 and 2 are shown in Figure 1. Figure 1a (sample 1) shows a single phase of ZnS with the face-centered cubic structure (JCPDS 80-0020). The broadening of peaks indicates that the sample consisted of very small particles.

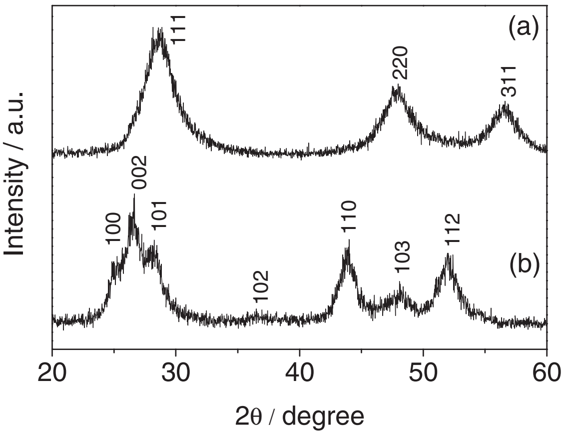

Figure 1. XRD patterns of samples 1 and 2. (a), sample 1; and (b) sample 2.

We estimated the diameter of ZnS nanoparticles using the Scherrer formula. According to the Scherrer formula, the broadening of XRD peaks is inversely proportional to the average crystallite size (L):

$$L = K\lambda/\beta\cos\theta$$

Where λ is the wavelength of X-ray; β is the line broadening contributed by the crystallite size; θ is the Bragg angle and K is the Scherrer constant. We used $K = 1$ in crystallite size calculation. The average crystallite size of ZnS (sample 1) calculated from three peaks (111), (220), and (311) was estimated to be $\approx$3.5 nm.

Figure 1b shows the XRD pattern of sample 2. It shows that sample 2 consisted of a single phase of CdS with the hexagonal structure (JCPDS No. 80-0006). The broadening of XRD peaks indicates that CdS crystallites were small in size. The average crystallite size of CdS calculated by the Scherrer formula was $\approx$7 nm.

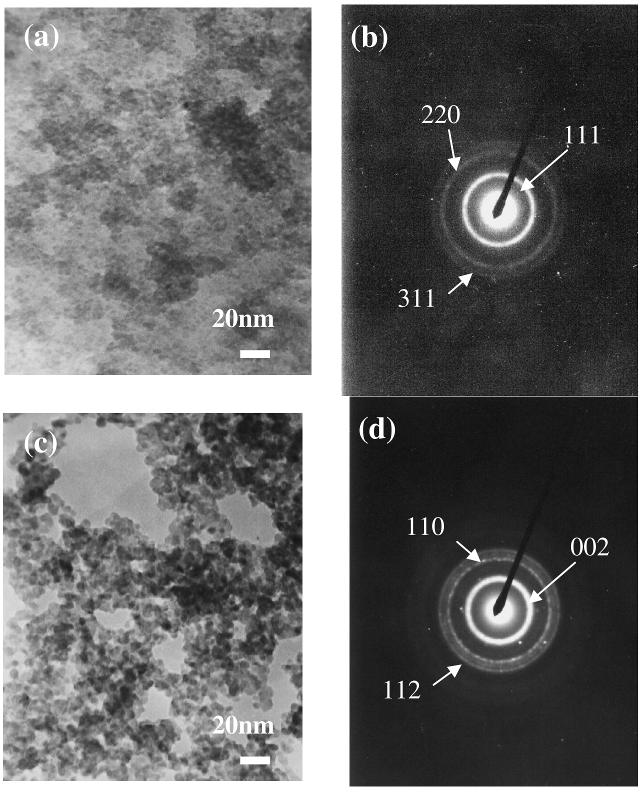

Figure 2. TEM micrographs of two typical samples. (a) sample 1; (b) electron diffraction pattern of sample 1; (c) sample 2; (d) electron diffraction pattern of sample 2.

The morphologies of the as-prepared products were investigated by transmission electron microscopy (TEM, JEOL JEM-2010). Figure 2a show a TEM micrograph for sample 1. One can see that ZnS sample was composed of ZnS nanoparticles with the spherical shape. ZnS nanoparticles were relatively uniform in size. The sizes of ZnS nanoparticles were consistent with the XRD result ($\approx$3.5 nm). Figure 2b shows the electron diffraction pattern of sample 1, from which one can see the polycrystalline diffraction rings. The three visible diffraction rings could be indexed to (111), (220), and (311) of the cubic ZnS, and the relative intensities of three diffraction rings are consistent with the XRD result (Figure 1a).

The TEM micrograph and electron diffraction pattern of sample 2 are shown in Figures 2c and 2d, respectively. One can see from Figure 2c that CdS sample consisted of spherical nanoparticles. The sizes of CdS nanopartcles were consistent with the result obtained from XRD ($\approx$7 nm). From the electron diffraction pattern shown in Figure 2d, one can see the polycrystalline diffraction rings. These diffraction rings could be indexed to the hexagonal CdS, consistent with the XRD result (Figure 1b).

It should be noted that no surfactant was used in the preparation of nanocrystalline metal sulfides. However, the sizes of metal sulfide nanoparticles were relatively uniform. In addition to its acting as a solvent, it is likely that the ionic liquid acted as a capping reagent or a surfactant. The detailed formation mechanism of metal sulfide nanoparticles in ionic liquids under the microwave heating needs to be further investigated.

In summary, nanoparticles of metal sulfides (ZnS and CdS) have been successfully synthesized using an ionic liquid ([BMIM]BF_4) under microwave heating at 100 °C for 10 min. As demonstrated by this successful example, the method may also be extended to prepare other elemental and compound nanostructures.

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