Sonochemical Synthesis of Nanocrystalline Copper Tellurides Cu_7Te_4 and Cu_4Te_3 at Room Temperature

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In this paper, we report a simple and clean method of producing nanocrystalline copper tellurides in an organic solvent system by high-intensity ultrasonic irradiation at room temperature. Cu_4Te_3 is prepared in a pure ethylenediamine system and Cu_7Te_4 is prepared in ethylenediamine with hydrazine hydrate. The products are characterized by X-ray powder diffraction (XRD), transmission electron microscope (TEM), and X-ray photoelectron spectra (XPS). Ultrasonic irradiation and the solvents are both important in the formation of products. The formation mechanism of the nanocrystalline tellurides under high-intensity ultrasonic irradiation is also discussed.

Introduction

With the increase of attention to nanostructured inorganic materials, reducing the reaction temperatures of synthesis has become a research goal for both chemists and materialists. Transition-metal tellurides represent a class of compounds that exhibit a wide range of physical and chemical properties.[1] In recent years the structures of a large number of tellurium-rich tellurides have been reported whose anionic networks are characterized by homonuclear Te−Te bonds. Tellurides are attractive materials for thermoelectric applications due to their very high thermopower values and ability to yield both p- and n-type materials by doping.[2] Traditionally, transition-metal tellurides were prepared by solid-state reaction at high temperature.[3] In the attempts to find processes for the preparation of tellurides at significantly lower growth temperatures, several methods such as aqueous solution by use of a very toxic and unstable reagent H_2Te,[4] the organic precursor method using unstable $CH_3Te{-}TeCH_3$ as a tellurium source,[5] and elemental reaction in liquid ammonia[6] were developed. Recently, a useful solvothermal route to nanocrystalline tellurides was also studied.[7] Efforts also aim to develop the existing experimental procedures into mature techniques that can be conducted at room temperature and are more controllable with respect to the product properties. Here, we report a new and simple technique for sonochemical synthesis of nanocrystalline copper tellurides (Cu_4Te_3 and Cu_7Te_4) in different solvent systems at room temperature.

The use of ultrasound to enhance chemical reaction in liquid−solid heterogeneous systems has become increasingly widespread. In heterogeneous, liquid−solid reactions, ultrasound has increased the reactivity of metal powders by as much as 100 000-fold.[8] A variety of nanostructured and often amorphous metals, alloy, and carbides has been produced from metal carbonyls under high-intensity ultrasonic irradiation.[9] Zinc sulfide[10] and amorphous nickel[11] were also prepared on silica microspheres by ultrasonic irradiation. To our knowledge, this is the first time that tellurides have been prepared by ultrasonic irradiation at room temperature.

Experimental Section

In a typical experimental procedure, Cu_4Te_3 can be prepared from a stoichiometric mixture of tellurium (0.300 g, 2.34 mmol) and $CuCl_2 \cdot 2H_2O$ (0.532 g, 3.13 mmol), all with nominal purity greater than 99.8%. The reagents were loaded into a 100-mL reactor that was then filled with anhydrous ethylenediamine up to 80% of the total volume. The reactor was designed to ensure that the horn tip was immersed into the solution consistently to the same depth (10 mm). The sealed reactor was kept in a circulating water bath to maintain the temperature of the bulk solution at 20 ± 5 °C and was irradiated with a high-intensity ultrasonic probe (Model, 1.5-cm Ti horn, 20 kHz, 100 W/cm^2) for 3 h. The precipitate was filtered and washed several times with distilled water and absolute ethanol to remove the byproducts. The product was dried in a vacuum

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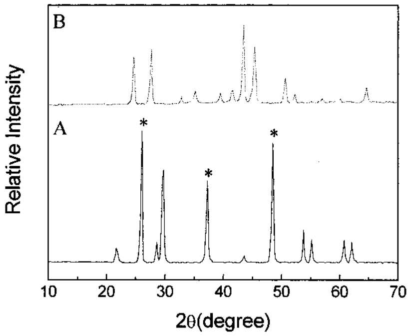

Figure 1. XRD patterns of (A) Cu_4Te_3 and (B) Cu_7Te_4 nanocrystals.

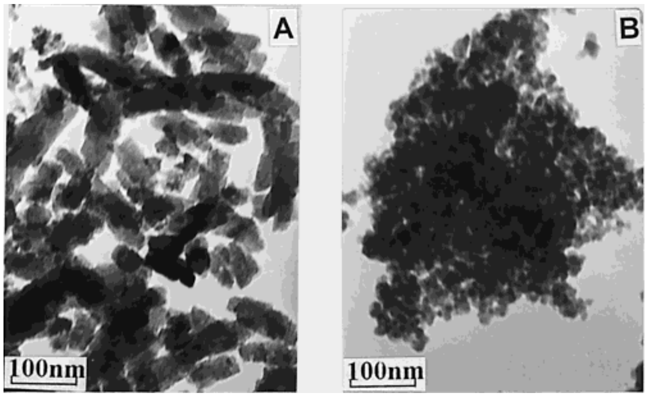

Figure 2. TEM images of (A) Cu_4Te_3 and (B) Cu_7Te_4 nanocrystals.

at 60 °C for 4 h. In the case of the preparation of Cu_7Te_4, the used reagents were the stoichiometric mixture of tellurium (0.205 g, 1.60 mmol) and $CuCl_2{\cdot}2H_2O$ (0.476 g, 2.80 mmol), and several drops of hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 85% v/v) were also added into the ethylenediamine solvent. The yields of Cu_4Te_3 and Cu_7Te_4 based on tellurium are about 87% and 91%, respectively.

The phases and the crystallographic structure of the products were determined by X-ray powder diffraction (XRD) using a Japan Rigaku D/max-γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). The scan rate of $0.05° \mathrm{s}^{-1}$ was applied to record the patterns in the 2θ range of 10°−70°. The morphology and size of prepared products were studied with transmission electron microscopy (TEM) images, which were taken on a Hitachi Model H-800, using an accelerating voltage of 200 kV. The X-ray photoelectron spectra (XPS) of the products were collected on an ESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Al Kα X-ray as the excitation source. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s to 284.60 eV.

Results and Discussion

The XRD patterns of Cu_4Te_3 and Cu_7Te_4 as prepared are shown in Figure 1, parts A and B, respectively. In each pattern, all peaks are consistent with those of a standard sample.[12] In Figure 1A, the reflections with a star have higher intensity than the corresponding reflections in the standard sample, indicating that the crystal has a preferential growth along some direction, which is consistent with the flakelike morphology shown in Figure 2A. The cell constants measured from the pattern in Figure 1B are $a = 8.335$ Å and $c = 7.211$ Å, which are close to the reported data for hexagonal Cu_7Te_4. Figure 2A shows that the sample Cu_4Te_3 synthesized in pure ethylenediamine appears to display flakes with nanosized widths and lengths. Meanwhile, the TEM image (Figure 2B) of Cu_7Te_4 synthesized in ethylenediamine in the presence of hydrazine hydrate shows the sample has spherical morphology with a diameter of ca. 12 nm, which is consistent with the result calculated from the half-width of diffraction peaks using the Scherrer formula. Because of the small dimensions and high surface energy of the crystals, it is easy for them to aggregate. Additional evidence for the quality and composition of the titled compounds was obtained by the X-ray photoelectron spectra (XPS). The XPS surveyed show that no obvious impurities, e.g., chloride ion, elemental tellurium, or tellurium oxide, could be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS (1 at. %).

In the processes of preparing tellurides, the ultrasonic irradiation plays an important role. Ultrasonic irradiation differs from traditional energy sources (such as heat, light, or ionizing radiation) in duration, pressure, and energy per molecule. The use of ultrasonic irradiation facilitates the reduction of tellurium to an active form that can react with metal cation Cu^+ or Cu^{2+} at room temperature. In ethylenediamine, which has N-chelating ligands, $CuCl_2{\cdot}2H_2O$ can dissolve and form a complex. This was supported by the fact that $CuCl_2{\cdot}2H_2O$ slowly dissolved after the addition of ethylenediamine and the solution color changed from transparent to light and then to dark blue. So in our process the system where the reaction is conducted is a heterogeneous system. In the liquid−solid solution, under ultrasonic irradiation the cavity collapsing near the extended solid surface of tellurium drives high-speed jets of liquid that impinge upon the surface. The impingement of the jet and related shock waves can create a localized erosion (which produces a newly exposed and highly reactive surface), improve mass transport, and cause particle fragmentation (which can substantially increase the surface of tellurium as brittle solids).[13] All these factors facilitate the reaction of tellurium with metal cations. When the experiments were made at room temperature with low intensity or without ultrasonic irradiation, the XRD measurements show that the reactions did not occur at all, even after prolonged periods of time. The high-intensity ultrasonic irradiation is necessarily fully responsible for these reactions.

The solvent also plays an important role in the formation of the titled products. Ethylenediamine was selected as the solvent due to its special properties, such as strong polarity, strong chelation, and certain solubility. As reported in the literature, this organic liquid can generate free radicals upon ultrasonic irradiation[14] and it is easy for ethylenediamine to be a donor solvent. The formation of tellurides might be through the attack of ethylenediamine on tellurium under high-intensity

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[12] JCPDS No. 42-1254 for Cu_4Te_3; JCPDS No. 18-456 for Cu_7Te_4.

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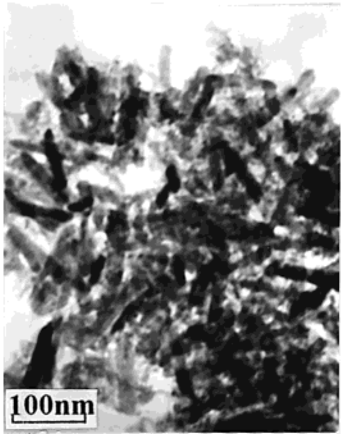

Figure 3. TEM image of released tellurium from solution.

ultrasonic irradiation. To improve on the understanding of the proposed mechanism, the following experiments were performed. Our experiments show that, under high-intensity ultrasonic irradiation, tellurium can form a solution with ethylenediamine, which remains stable in an open container for 1 day and then releases tellurium. Moreover, this released tellurium is in the form of nanorods with different widths and lengths, as shown by the TEM image in Figure 3. Compared with the raw material of tellurium with its microsize, there is a sharp decrease in the size of tellurium. However, the microsize particles cannot be significantly decreased in size under high-intensity ultrasonic irradiation, even after several hours of irradiation.[15] So the nanosized tellurium might be formed by the slow release from the ethylenediamine solution. However, when $CuSO_4 \cdot 5H_2O$ was used to substitute $CuCl_2 \cdot 2H_2O$, we could not obtain any copper tellurides under the same conditions. This might be because of the fact that the halogen ion Cl^- has a certain coordinative ability but the SO_4^{2-} has not. Certainly, the corrdinative ability of the halogen ions or their reductibility or the coaction leads to the reaction has to be further studied. In the crystallization of final products, ethylenediamine also plays an important role. Products prepared by high-intensity ultrasonic irradiation are often in an amorphous form,[9,11] but the products synthesized in our experiments are both crystalline. Although ultrasound provides extraordinary heating and cooling rates,[16] ethylenediamine can provide reaction conditions mild enough to enable molecular-building blocks to participate in subsequent formation of the solid-state phase and greatly enhance crystallization.[17] Moreover, the ethylenediamine system is especially promising for the synthesis of metal polychalcogenides[18] because the very mild solution medium stabilizes the polychalcogen building blocks and allows Q_y^{2-} ($y \geq 2$) ions to incorporate and remain intact in the final structure. To confirm the importance of ethylenediamine as a solvent in the formation of the products, the reactions were also performed in other solvents such as benzene and ethanol. The results, which were detected by XRD, showed that no copper telluride was obtained in both cases.

Under high-intensity ultrasonic irradiation, in the pure ethylenediamine system what we get is Cu_4Te_3, which is different from the product Cu_7Te_4 prepared by the solvothermal process under the same solvent system.[7] In the solvothermal process, high temperature and pressure increased the reductive atmosphere and reduced the major Cu^{2+} to Cu^+ to form Cu_7Te_4. In the ultrasonic irradiating process, to get Cu_7Te_4, reducing agent must be added. In our experiments, Cu_7Te_4 can be obtained by adding several drops of hydrazine hydrate into the ethylenediamine system. As a reducing agent, hydrazine hydrate can reduce the major Cu^{2+} to Cu^+ to form Cu_7Te_4.

The addition of hydrazine hydrate has great influences not only on the phase of final products but also on the morphology and size of final products. Hydrazine hydrate has a higher dielectric constant and viscosity. For the preparation of well-dispersed particles, it is helpful to use solvents with a larger dielectric constant.[19] During the formation of the final product, the competition between particle growth and nucleation is partially controlled by diffusion. For high-viscosity solutions, the rate of diffusion is low and the Cu_4Te_3 or Cu_7Te_4 can form a new nucleus before they migrate to the surface of the nuclei. The time of nucleation and length of the growth period of nuclei in different solution systems are not the same, giving particles with different sizes at the end of the growth process. In the highly viscous solution, the rate of diffusion is slow, resulting from the addition of the high viscosity of hydrazine hydrate. Therefore, the size of the product prepared in ethylenediamine with hydrazine hydrate is much smaller than that prepared in pure ethylenediamine, as shown in Figure 2. The formation of the flakelike morphology of Cu_4Te_3 is related to the structure of ethylenediamine.[20]

Conclusion

In conclusion, nanocrystalline copper tellurides Cu_4Te_3 and Cu_7Te_4 have been successfully prepared in the ethylenediamine system under high-intensity ultrasonic irradiation at room temperature. The presence of hydrazine hydrate influences the phase of the final product and makes well-dispersed nanocrystals. This inexpensive and extremely reliable method can be easily controlled and is expected to be applicable to the preparation of other nanosized inorganic compounds. Further studies on the use of ultrasonic irradiation to prepare other tellurides are underway.

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