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Mild Solvothermal Synthesis and TEM Investigation of Unprotected Nanoparticles of Tin Sulfide

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Introduction

IV−VI-semiconductor compounds such as PbSe, SnSe, and SnS have been playing an important role in different areas of materials science for several decades.[1] The orthorhombic Herzenbergite modification of SnS (like SnSe) possesses a layered structure consisting of six-membered rings, a structural analogue of black phosphorus.[2] SnS is a narrow band gap semiconductor with an optical band gap of 1.08 eV, which is ideal for photoelectric energy conversion. SnS films have shown a conversion efficiency in photovoltaic devices similar to the one found for silicon films (up to 25%).[3−5] Given the well-known dependence of optical and electronic properties of semiconductors on particle size,[6] unprotected SnS nanoparticles with a narrow size distribution would be very attractive for spectroscopic investigations as well as for possible applications. As the grain sizes observed in thin films of SnS are in the nanometer range,[3−5] applications could include liquid-phase epitaxy or dip coating of glass or metal supports with finely dispersed nanoparticles of SnS.

Surprisingly, very few attempts to synthesize such unprotected SnS nanoparticles have been reported in the literature. Reaction of tin powder with sulfur in liquid ammonia or ethylenediamine resulted in neither single-phase materials nor nanoscale particles.[7,8] Thermolytic approaches from organotin compounds that led to β-SnS (Herzenbergite) single-phase samples were reported but produced either very large grain sizes (>200 nm)[9] or nanophase SnS that seemed to contain amorphous material.[10] SnS thin films with nanometer grain sizes have been prepared by deposition from an aqueous chemical bath[3] or by CVD methods.[11]

In this paper, we present a one-pot synthesis of SnS nanoparticles from in situ activated tin metal and elemental sulfur in diethyleneglycoldimethylether (diglyme) at 160 °C. The synthesis does not involve any templates or surface-protecting additives such as thiols or phosphanes and does not require the use of an autoclave.

Experimental Section

All manipulations were carried out under dry, oxygen-free argon, except where stated otherwise. Li[Et_3BH], 1 M in tetrahydrofuran (THF), and diethyleneglycoldimethylether (anhydrous) were purchased from Aldrich, and $SnCl_2$ (anhydrous) and sulfur were purchased from Merck. All chemicals were used as obtained. THF was obtained from Merck and distilled over CaH_2 under argon.

Powder X-ray diffraction data were collected using a STOE-Stadi P diffractometer (germanium monochromator, Cu Kα radiation, $\lambda =$ 154.056 pm, linear position sensitive detector, Si as an external standard).

The sample was characterized by high-resolution electron microscopy (HREM) and selected area electron diffraction (SAD). The crystallites were dispersed in *n*-butanol. One drop of the suspension was placed on a perforated carbon/copper net, which was dried carefully, leaving the crystallites in a random orientation. The electron microscopy studies were performed using a Philips CM30/ST instrument (spherical aberration constant $C_S = 1.15$ mm) equipped with a LaB_6 cathode. At 300 kV, the point resolution is 0.19 nm. SAD patterns were obtained using a diaphragm that limited the diffraction of the selected crystallite to a region of 125 nm in diameter. The kinematical electron diffraction patterns were calculated with the program EMS.[12] EDX analysis was carried out with a Philips XL30 ESEM scanning electron microscope (acceleration voltage, 25 kV; SE mode detection). For the analysis, a small amount of SnS powder was placed on an adhesive graphite foil.

Synthesis of SnS Nanoparticles. A 190 mg sample (1.0 mmol) of $SnCl_2$ was dissolved in 80 mL of diglyme, and 2.0 mL of a 1 M solution of Li[Et_3BH] in THF was added dropwise.[13] Finely divided brownish-black tin precipitated during the addition. After the H_2 evolution ceased, the reaction mixture was stirred for an additional 10 min. Then, 32 mg (1.0 mmol) of elemental sulfur was added, and the reaction mixture was heated to 160 °C for 24 h. It was allowed to cool to room temperature, and the black precipitate was filtered off and washed with 2 × 10.0 mL of THF. The SnS nanoparticles were dried in vacuo and stored in air at room temperature.

Results and Discussion

Crystalline, single-phase β-SnS nanoparticles with an average size of 20 × 40 nm were obtained by reaction of the elements in the polyether diglyme. The activated, nanoscale tin used in this synthesis was generated in situ by the reduction of tin(II) chloride with lithium triethylboron hydride.[13] As prepared, tin showed clean and complete conversion to Herzenbergite SnS when reacted with a solution of elemental sulfur in diglyme solvent. When we tried to react commercial tin powder with elemental sulfur in diglyme at 160 °C, no conversion to SnS was observed and the elements remained unreacted. Thus, one can conclude that the small particle size and the large surface area of the nanocrystalline tin powder are indispensable for a low-temperature synthesis.

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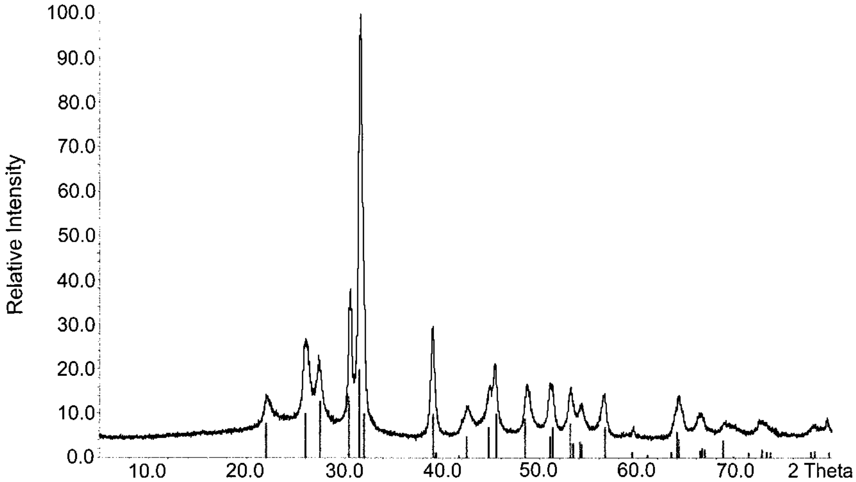

Figure 1. Powder X-ray diffraction pattern for SnS nanoparticles with reflections indexed for Herzenbergite (JCPDS 39−354).

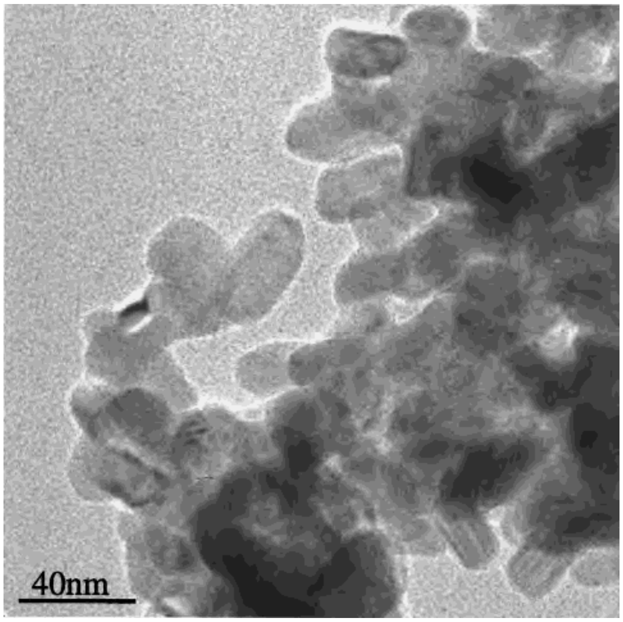

Figure 2. Typical TEM micrograph of SnS nanocrystals.

Figure 1 shows the powder X-ray diffraction pattern for the SnS particles indexed with the diffraction peaks of SnS as reported in JCPDS 39−354.[2] All reflections were indexed and assigned to orthorhombic β-SnS (*Pbnm*, $a = 4.305(3)$ Å, $b = 11.262(4)$ Å, $c = 3.976(2)$ Å, $V = 192.77(12)$ Å^3), and no other crystalline phase is observable. A mean crystallite size of 18−20 nm was derived from the reflections using the Scherrer equation.[14]

EDX analysis of the nanoparticles with a scanning electron microscope (SEM) confirmed a Sn:S ratio of 1:1. No residual chloride could be detected.

To confirm the absence of amorphous material (either amorphous SnS or a different product), we investigated the black powder under the transmission electron microscope (TEM). A typical TEM micrograph of our SnS particles is shown in Figure 2. All particles exhibited a similar shape. Electron diffraction (SAD) was carried out in order to check the structure type of the nanocrystals on a single-particle level. The SAD patterns obtained in a series of tilting experiments could be indexed completely on the basis of the cell of Herzenbergite and thus confirm that Herzenbergite is the only crystalline compound present in the sample. No amorphous particles or extended amorphous regions in the nanocrystals could be observed. The dimensions of the oval nanocrystals were in the range of 20−40 nm. The majority of the nanocrystals did not exhibit lattice defects, and electron diffraction led to sharp Bragg reflections only (Figure 3). These patterns showed good agreement with calculated kinematical patterns as shown for the zone axis [101] in Figure 3. Only in rare cases was additional diffuse scattering present in the SAD patterns. For the zone axis [101], diffuse streaks along b^* between the Bragg reflections were found. As SnS crystallizes in the layered-GeS-type structure with the layers stacked along the b axis,[2] the streaks can most likely be attributed to stacking faults in this direction.

The low-temperature synthesis presented here shows the good applicability of activated, but isolable, tin metal in the direct synthesis of nanocrystals of a IV−VI semiconductor from its elements. So far, elemental-direct reactions[15] leading to nanoparticles have been reported for II−VI semiconductors such as CdSe, CdS, and ZnSe and required the use of an autoclave and strongly coordinating tertiary amines.[15,16] A solvothermal synthesis of InSb that involves activated antimony as an intermediate is also available but does not operate cleanly below 300 °C.[17] In contrast to these known procedures, our approach does not aim at the activation of the chalcogen or the group 15 element but at the activation of the metal.[18]

Summary

Reaction of activated tin and sulfur in diglyme provides a convenient route for the one-pot synthesis of unprotected SnS nanoparticles 20−40 nm in size. Single-phase, highly crystalline material was obtained under mild thermal conditions and at standard pressure.

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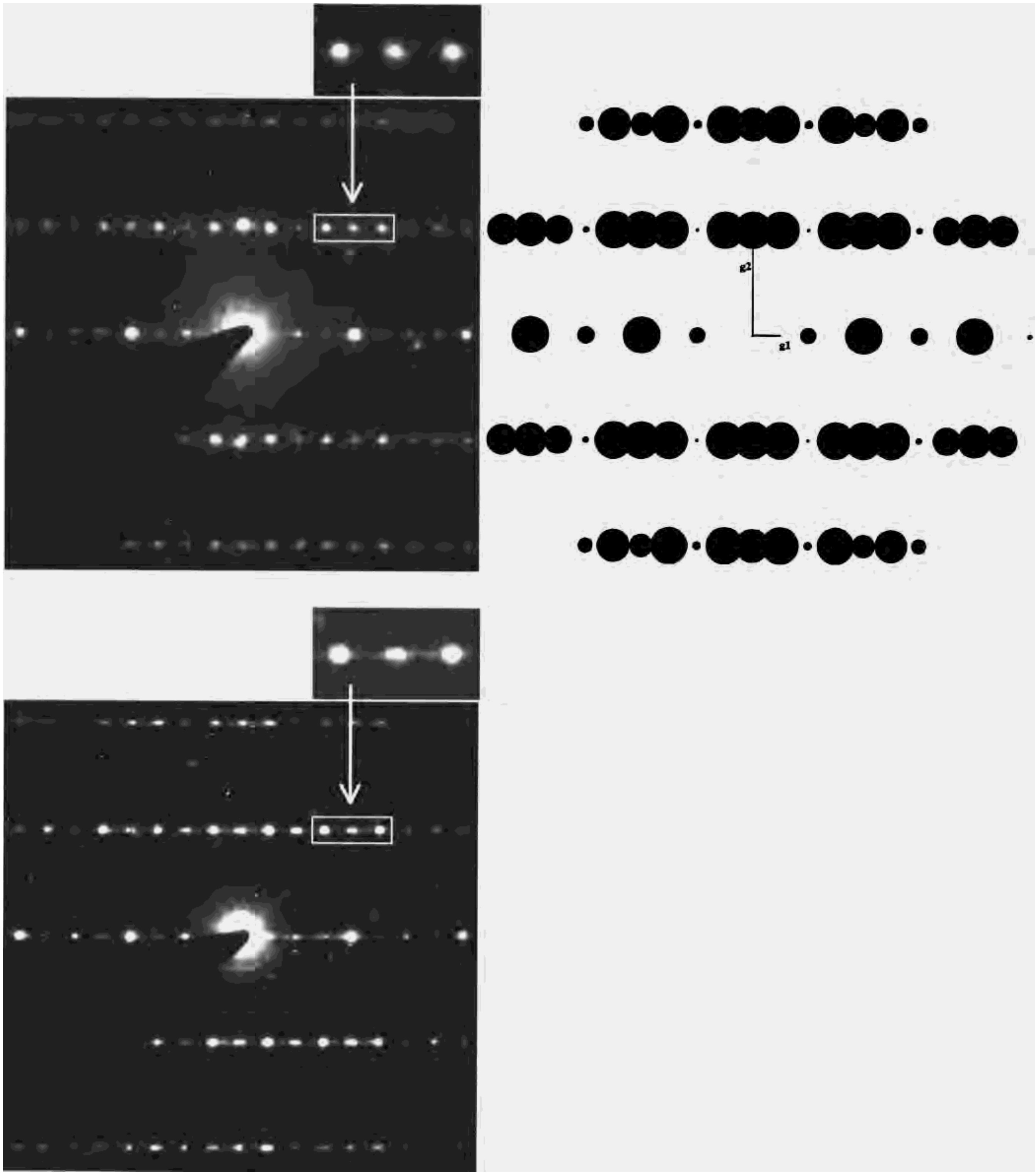

Figure 3. SAD patterns, zone axis [101]. Top left: undistorted crystallite. The marked region of the pattern is enlarged. Top right: kinematical simulation. The directions g1 and g2 correspond to *b** and [10$\bar{1}$], respectively. Bottom left: distorted crystallite. The marked region (enlarged section) shows diffuse scattering extended in *b** between the Bragg reflections.

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Supporting Information Available: An HREM lattice image of an undistorted nanoparticle of SnS, zone axis [101]. This material is available free of charge via the Internet at http://pubs.acs.org.

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