JOURNAL OF MATERIALS SCIENCE **39** (2004) 659–661

Control of the sizes of zinc sulfide particles by extractant

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Over the past decade, considerable interest has been given to the II–VI nanostructured semiconductors because of their important nonlinear optical properties, luminescent properties, quantum size effects and other important physical and chemical properties [1–7], and much progress has been made in the synthesis and characterization of these materials [8–10]. ZnS is a II–VI semiconductor with a large direct band gap in the near-UV region, and ZnS has many uses in blue light emitting diodes, electroluminescent displays, cathodoluminescent displays and multilayer dielectric filters, light guiding in integrated optics, IR antiflection coatings and solar cell [11, 12].

It has been shown that the sizes of particles and its distribution play an important role in the properties and applications of materials. Thus, it is important to synthesize particles with the desired size and a narrow distribution in an easily-to-control condition.

In order to obtain particles with desired size, a variety of methods including hydrothermal method, colloid chemistry method, solid state method and so on [13–17], have been developed for the chemical preparation of relatively monodispersed nanoparticles of various semiconductor materials. Although considerable progress has been made in the controlled synthesis of II–VI semiconductor crystallites, the control of the size and shape of particles still be the main problem in preparation of these materials. In this paper, the extractant (primary amine N1923) was used to control the size of ZnS and a new method to prepare materials, extraction-solvothermal, is proposed.

The primary amine N1923 ($R_1R_2CHNH_2$) was purified as described in literature [18]. The other chemicals were of analytical grade. The procedure to prepare ZnS is as follows: The negative ions of zinc, for example $ZnCl_4^{2-}$, were formed by adding NaCl into the $ZnCl_2$ solution in which the pH value is 3; and zinc ions were extracted into organic phase by primary amine N1923 which is pretreated according to the different experimental conditions; then the organic phase was transferred into the Teflon lined stainless autoclave; after the absolute ethanol and CS_2 were added into the autoclave, the autoclave was heated at 180 °C for 18 h.

The structures of products were investigated with a Rigaku D/Mas-γA X-ray diffractometer. The size and shape were observed under a JEM-100CX II transmission electron microscopy.

Li *et al.* [19] have studied the extraction of zinc (II) from aqueous hydrochloric media by primary amine N1923. Two possible extraction mechanisms may be expressed as follows:

(a) at low acidities and no acidified primary amine N1923

$$2RNH_2(o) + ZnCl_2(a) \leftrightarrow (RNH_2)_2ZnCl_2(o)$$

(b) when the primary amine N1923 was acidified and at high Cl^- concentraction

$$ZnCl_4^{2-}(a) + 2RNH_3^+(o) \leftrightarrow (RNH_3^+)_2ZnCl_4^{2-}(o)$$

Then the extracted complex in organic phase reacted with CS_2 at 180 °C for 18 h and ZnS nanoparticles were obtained.

X-ray diffraction patterns of ZnS prepared at three different typical conditions of extractant are shown in Fig. 1. They reveal that pure zinc blende nanocrystallite were obtained in the extraction-solvothermal process. Although some intense peaks of the hexagonal phase may present at the same d values, no unique peaks of hexagonal phase, such as (100) at $2\theta = 26.9\,°(d = 3.310$ Å) and (101) at $2\theta = 30.5\,°(d = 2.926$ Å), were found in the ZnS diffraction pattern, indicating the absence of hexagonal phase. The cell parameter was calculated and a was found to be 0.54 nm, which is in good agreement with the literature value [20]. The average crystallite sizes can be calculated from the half-width of the diffraction peaks using Debye-Scherrer formula, $D = \alpha\lambda/\beta\cos\theta$, where D is the mean particle size, α is a geometric factor (equal to 0.89), λ is the X-ray wavelength (1.54178 Å), β is the half-width of diffraction peak, and θ is the degree of the diffraction peak. Here, θ corresponding to (111) plane is selected. Estimating from the formula, the average crystallite sizes of the ZnS particles prepared at three different typical conditions are given in Table I.

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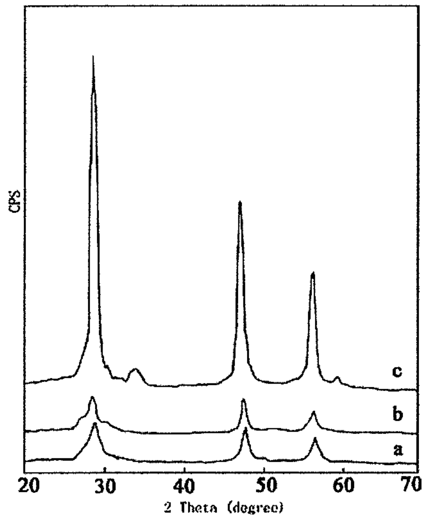

Figure 1 XRD patterns of ZnS particles at three different typical conditions of extractant (primary amine N1923). The acidified degree of primary amine N1923 is 0% (a), 50% (b), and 100% (c) respectively. The molar ratio of solvent and ethanol: n-heptane/ethanol = 1/1.

The transmission electron images of the sample prepared at different acidified conditions are shown in Fig. 2. From Fig. 2, it can be seen clearly that the morphology of the particles is different at different conditions. The relationship between the sizes of particles and the acidified degree of extractant is shown in Fig. 3.

TABLE I Different sizes of ZnS at different conditions of extractants

Different acidified degrees of extractants	0%	50%	100%
D_{XRD}	3.2 nm	4.1 nm	14.4 nm
D_{TEM}	10 nm	40 nm	3.45 μm

D_{XRD} represents crystallite size—the size of ZnS by XRD (calculated by Debye-Sherrer formula).

D_{TEM} represents particle size—the size of ZnS by TEM.

The sizes were listed in Table I. The particle size observed in TEM micrograph is much larger than that of the crystallite estimated from the Debye-Sherrer formula. This indicates that each particle observed under TEM may be aggregates of fine crystallites, whose sizes were determined by XRD technique. Therefore, we may call the size resulted from TEM images as "particle size," and the size calculated from XRD data as "crystallite size." As shown in Table I, both the particle size and the crystallite size increase obviously with the increase of acidification degree of N1923. The dramatic increase of the particle size when N1923 was totally acidified indicates that ZnS crystallites are apt to aggregate under this condition. It was also found that particles prepared with half-acidified N1923 are very uniform and well dispersed. All the above results show that the acidification degree of the extractant N1923 affects the particle size greatly.

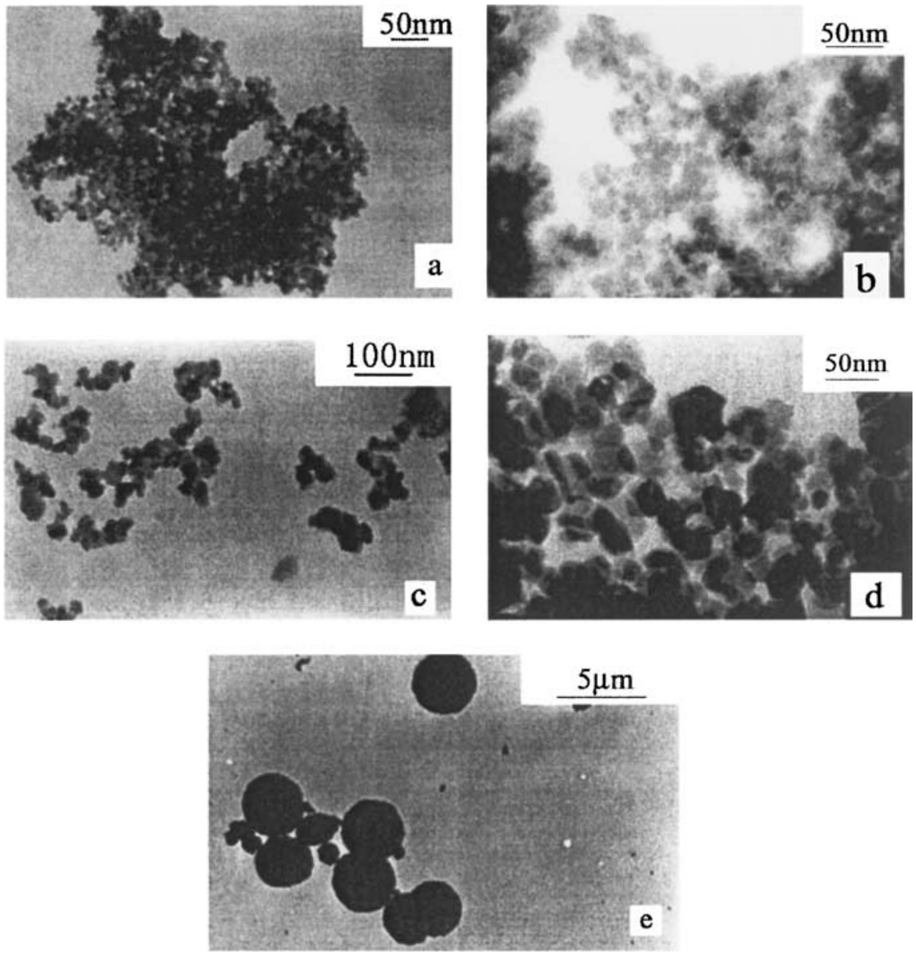

Figure 2 TEM micrographs of the ZnS prepared at different acidified conditions of extractants. The acidified degree of primary amine N1923 is 0% (a), 10% (b), 50% (c), 70% (d) and 100% (e) respectively.

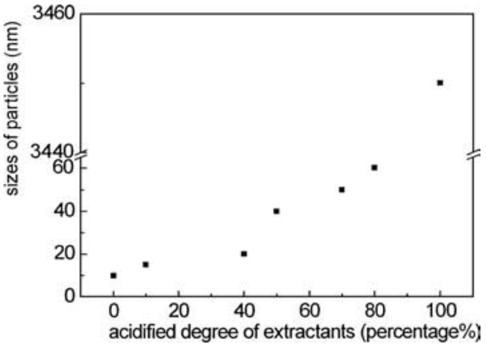

Figure 3 The relationship between the sizes of particles and the acidified degree of extractant.

In our previous work [21], we have demonstrated that both pure and acidified primary amine N1923 tends to form aggregates of micelles in organic solution. But the aggregation behavior is different. The micelles can somewhat control the size and shape of the particles formed in them [22]. However, the difference of the aggregation properties may be one factor that influences the size of the particles. Another factor that may affect the particle size is that amine group binds tightly to the surface of ZnS particles, hence, tremendously restrict the aggregation of the particles. But the ammonium group, which bears a positive charge and has one electron pair, cannot bind to ZnS. Therefore, smaller particles are formed under the lower acidification degree of the extractant. In addition, the concentration of sulfide ions is determined by the acidity of the solution. At lower acidity, the sulfide concentration is higher, and leads to the formation of more crystal seeds simultaneously. And finally, smaller particles are resulted.

ZnS nanoparticles can be synthesized by a new pathway, extraction-solvothermal method, with primary amine N1923 as the extractant. The size of particles depends greatly on the acidification degree of the extractant.

Acknowledgment

This work was supported by the National Nature Science Foundation (Project No. 20171029 and No. 20001001).

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Received 10 January 2002
and accepted 7 July 2003