

DEPENDENCE ON GRAIN SIZE AND MORPHOLOGY OF ZINC SULFIDE PARTICLES BY THE SYNTHESIS ROUTE*

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Received December 21, 2004

There were synthesized ZnS nanoparticles by different routes, using thiourea as source for sulfide ion. The nanoparticles were studied by TEM having in view the correlation between starting materials, synthesis route, grain size and grain size distribution.

Key words: zinc sulfide, nanoparticles, TEM, thiourea.

1. INTRODUCTION

In the past few decades, metal chalcogenides have been extensively studied because of their important physical chemical properties and their great potential application in electronic, optical, and superconductor devices [1–4].

Nanoparticles are of great interest due to their extremely small size and large surface-to-volume ratio, which lead to both chemical and physical differences in their properties, compared to bulk of the same chemical composition. The physical properties of semiconductor nanocrystallites are dominated by the spatial confinement of excitations (electronic and vibrational). Quantum confinement, the widening HOMO LUMO gap with decreasing crystallite size, and its implications for the electronic structure and photophysics of the crystallites have generated considerable interest. The semiconductor nanoparticles may find applications in nonlinear optical devices, photocatalysis, etc. [5–7].

Being a compound semiconductor, zinc sulfide has found many applications in various fields, such as phosphors, solar cells, and IR window. Zinc sulfide can be used as thin film or in the form of particles. It has been shown that the particle size and its distribution play an important role in applications. Thus, it is an important challenge to synthesize particles with small size and monodistribution, especially in the nanometer range [8]. To obtain nanometer-sized particles, a

* Paper presented at the 5th International Balkan Workshop on Applied Physics, 5–7 July 2004, Constanta, Romania.

variety of methods has been proposed, including precipitation in aqueous and organic media [9], solid-state reaction [10, 11], thermal decomposition [12, 13], solvothermal synthesis [14–16], and microemulsion method [17].

In our previous work, we had prepared and analysed ZnS nanoparticles obtained using thiourea as source for sulfide ion [18]. Having in view these results, we studied the influence of reaction medium on the morphology and dimension of particles.

In this paper are described the synthesis and analysis of zinc sulfide nanoparticles obtained by two syntheses routes, using hydrothermal method, in different reaction conditions. The morphology, particle size and distribution of nanoparticles depend on synthesis strategy.

2. EXPERIMENTAL

2.1. SYNTHESSES

All the reagents and solvents were purchased from commercial sources and used as received.

2.2. PREPARATION OF ZnS

Sample **1** of ZnS. 0.38 g (5 mmol) thiourea and 0.01 g (0.04 mmol) sodium palmitate were added into an aqueous solution containing 1.10 g (5 mmol) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The resulting mixture was heated under continuous stirring for 4 hours. A white precipitate was separated. It was isolated by vacuum filtration, washed with water and dried. Elemental analysis: Calc.: Zn, 67.01%; S, 32.99%. Found: Zn, 67.53%; S, 32.46%. IR spectrum (cm^{-1} , KBr): 692m; 473 m.

Sample **2** of ZnS. 0.38 g (5 mmol) thiourea and 0.10 g (0.3 mmol) tetra-*n*-butylammonium bromide were added into an aqueous solution containing 1.10 g (5 mmol) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. The resulting mixture was heated under continuous stirring for 4 hours. A white precipitate was separated. It was isolated by vacuum filtration, washed with water and dried. Elemental analysis: Calc.: Zn, 67.01%; S, 32.99%. Found: Zn, 67.75%; S, 32.23%. IR spectrum (cm^{-1} , KBr): 680 m; 480 m.

2.3. PHYSICAL MEASUREMENTS

Infrared spectra were recorded with a BRUKER Vector 22 FTIR spectrometer from KBr pellets, in the 400–4000 cm^{-1} range.

The TEM's were made on the Philips CM 120 transmission electron microscope operated at 100 kV, with 2 Å resolution.

3. RESULTS AND DISCUSSION

Zinc sulfide was prepared by heating a mixture of zinc acetate and thiourea, in the presence of a cationic/anionic surfactant. Surfactants can have an important effect on the morphology of ZnS particles [1]. Although an extended study of controlling morphology by use of surfactants is needed, the morphology of particles seems to be in a close relation with the structure of surfactant used.

In the aim to prove the influence of surfactants on the morphology of nanoparticles, we used two surfactants: an anionic surfactant (sodium palmitate) and a cationic surfactant (tetra-*n*-butylammonium bromide).

SAED (Selected Area Electron Diffraction) patterns on samples **1** and **2** confirm presence of ZnS cubic structure.

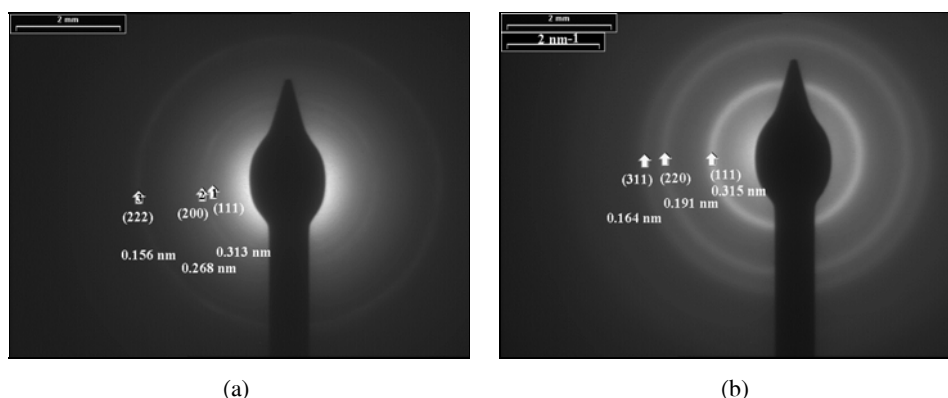


Fig. 1. – SAED images of a nanoparticle indexed using a cubic structure (F-43m) $a = 0.541$ nm (up arrow): (a) ZnS (1); (b) ZnS (2).

HRTEM (High-Resolution Transmission Electron Microscopy) can provide structural information at better than 0.2 nm spatial resolution. In most crystalline inorganic materials, including ceramics, semiconductors and metals, the positions of individual atomic columns can be resolved, at least in low-index zones [19]. The HRTEM image was used for determination of ZnS structure.

The morphologies of particles were studied using transmission electron microscopy.

The size of primary nanoparticles can be determined from imaging by TEM. This technology is more direct than X-ray line broadening and less likely to be affected by experimental errors and/or other properties of the particles such as strain or a distribution in the size of lattice parameter [3]. Fig. 3.a., respective 4.a., depicts the bright field TEM micrographs of ZnS samples.

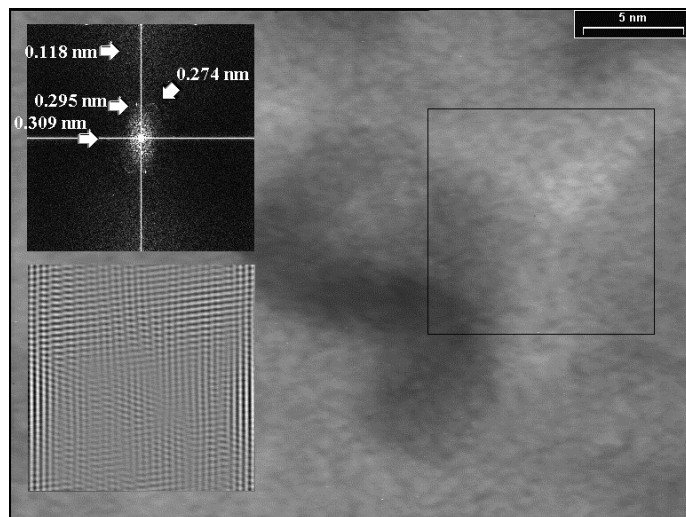


Fig. 2. – HRTEM image of ZnS (1) single nanocrystal. Left inserts present FFT representation of selected area (up) and filtered image obtained using a blob type filter in Fourier space that select only point indicated by arrow in previously image.

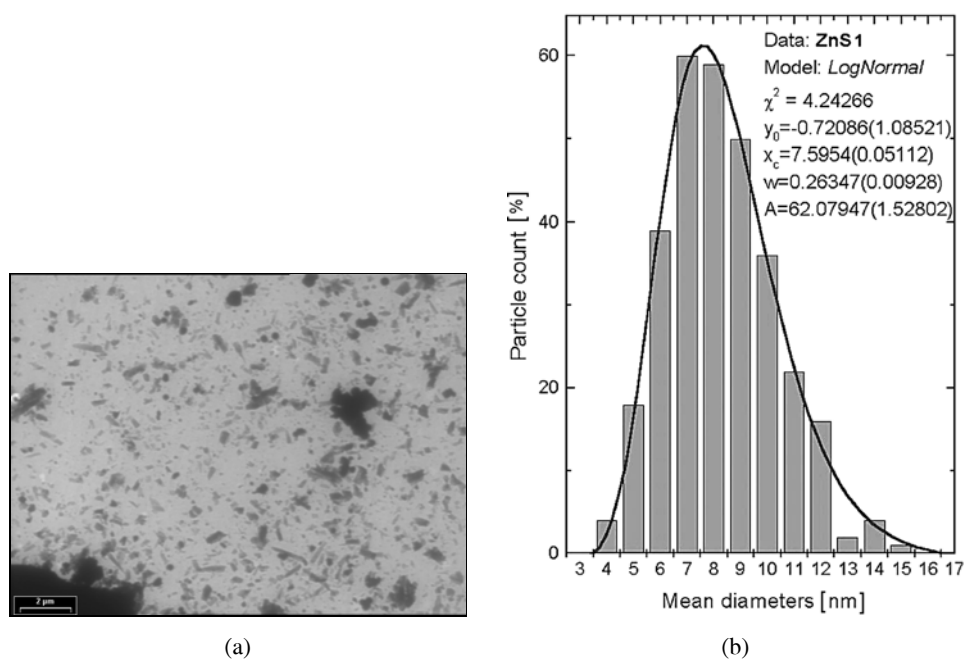


Fig. 3. – (a) TEM image for ZnS, sample 1; (b) Mean particle size and particle distribution for ZnS, sample 1.

The Fig. 3.a indicates that most particles are fine and plane. As shown, the particles of ZnS (1) are uniform and the diameters are in range of 4.97–19.46 nm with a mean diameter of 8.88 nm.

Fig. 3.b. presents lognormal distribution curve for mean diameter of ZnS (1) nanoparticles. Mean diameter of particle is evaluated by arithmetic mean of diameters measured at different angle (0, 15, 30, ...180 deg). The lognormal function used for fit the experimental curves are given by:

$$y = Ae^{-\frac{\ln^2(x/x_c)}{2w^2}}$$

where A is an arbitrary constant related to particle number, x_c represents the distribution maximum and w is strong correlated with particle diameter dispersion.

The Fig. 4 indicates that particles of ZnS (2) are very fine, spherical and uniform. The diameters are in range of 1.34–5.86 nm with a mean diameter of 2.67 nm.

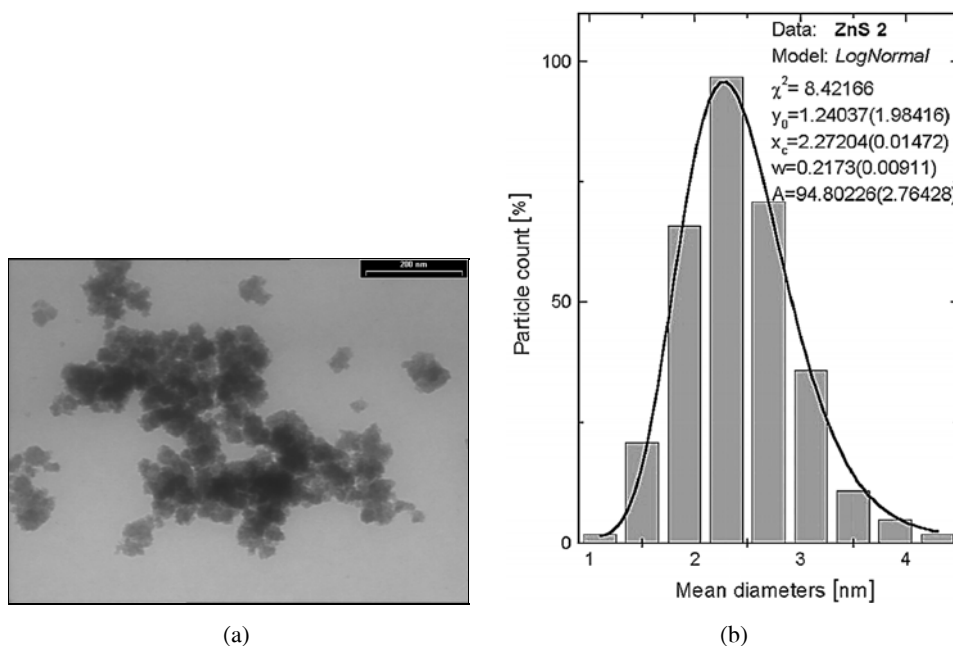


Fig. 4. – (a) TEM image for ZnS, sample 2; (b) Mean particle size and particle distribution for ZnS, sample 2.

4. CONCLUSIONS

Zinc sulfide nanoparticles have been successfully obtained in a simple aqueous system, in the presence of surfactants, using $\text{Zn}(\text{CH}_3\text{COO})_2$ and

thiourea as the initial materials. The presence and nature of surfactant could affect the morphology, particle size and distribution of the final product particles. In the presence of sodium palmitate, the obtained nanoparticles are plane, almost hexagonal. Using tetra-*n*-butylammonium bromide, there were obtained spherical and very small ZnS nanoparticles, which can be include in the nanocrystals category. Both samples are more uniform than in absence of surfactants. The particles of minimum size were obtained in the presence of tetra-*n*-butylammonium bromide.

REFERENCES

1. Y. Liu, J. Zhan, M. Ren, K. Tang, W. Yu, Y. Qian, Hydrothermal synthesis of square thin flake CdS by using surfactants and thiocarbohydrate, *Mater. Res. Bull.*, **36** (2001), 1231–1236.
2. Q. Yang, K. Tang, C. Wang, D. Zhang, Y. Qian, The synthesis of SnS₂ nanoflakes from tetrabutyltin precursor, *J. Sol. State Chem.*, **164** (2002), 106–109.
3. Y. Wang, C. Ma, X. Sun, H. Li, Preparation of nanocrystalline metal oxide powders with the surfactant - mediated method, *Inorg. Chem. Comm.*, **5** (2002), 751–755.
4. E. Benavente, M. A. Santa Ana, F. Mendizabal, G. Gonzalez, Intercalation chemistry of molybdenum disulfide, *Coord. Chem. Rev.*, **224** (2002), 87–109.
5. M. C. Brelle, C. L. Torres-Martinez, J. C. McNulty, R. K. Mehra, J. Z. Zhang, Synthesis and characterization of Cu_xS nanoparticles. Nature of the infrared band and charge-carrier dynamics, *Pure Appl. Chem.*, **72** (2000), 101–117.
6. C. B. Murray, D. J. Norris, M. G. Bawendi, Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites, *J. Am. Chem. Soc.*, **115** (1993), 8706–8715.
7. L. Li, J. Hu, W. Yang, A. P. Alivisatos, Band Gap Variation of Size- and Shape-Controlled Colloidal CdSe Quantum Rods, *Nano Letters*, **1** (2001), 349–351.
8. L. P. Wang, G. Y. Hong, A new preparation of zinc sulfide nanoparticles by solid state method at low temperature, *Mat. Res. Bull.*, **35** (2000), 695–701.
9. D. Gallagher, W. E. Heady, J. M. Racz, R. N. Bhargava, Homogeneous precipitation of doped zinc sulfide nanocrystals for photonic applications, *J. Mater. Res.*, **10** (1995), 870–875.
10. T.-Y. Zhou, X.-Q. Xin, *Nanotechnology*, **15** (2004), 534–536.
11. L. P. Wang, G. Y. Hong, A new preparation of zinc sulfide nanoparticles by solid-state method at low temperature, *Mater. Res. Bull.*, **35** (2000), 695–701.
12. H. Kim, W. Sigmund, Zinc sulfide nanocrystals on carbon nanotubes, *J. Cryst. Grow.*, **255** (2003), 114–118.
13. D. Moore, C. Ronning, C. Ma, Z. Wang, Wurtzite ZnS nanosaws produced by polar surfaces, *Chem. Phys. Lett.*, **385** (2004), 8–11.
14. Y. Dong, Q. Peng, Y. Li, *Inorg. Chem. Comm.*, **7** (2004), 370–373.
15. Z.-P. Qiao, G. Xie, J. Tao, Z.-Y. Nie, Y.-Z. Lin, X.-M. Chen, Coordination Polymer Route to Wurtzite ZnS and CdS Nanorods, *J. Sol. State Chem.*, **166** (2002), 49–52.
16. Q. T. Zhao, L. S. Hou, R. A. Huang, S. P. Gu, Optical Properties and Structure Analyses of Zinc Sulfide Nanorods, *Chinese Phys. Lett.*, **20** (2003), 1496–1497.
17. J. Xu, Y. Li, Formation of zinc sulfide nanorods and nanoparticles in ternary W/O microemulsions, *J. Coll. Interface Sci.*, **262** (2003), 275–281.
18. A. Dumbrava, V. Ciupina, G. Prodan, Characterization of zinc sulfide nanoparticles by transmission electron microscopy, 4th Aegean Analytical Chemistry Days, Turkey, in press.
19. P. R. Buseck, J. M. Cowley, L. Eyring, Eds.: *High-Resolution Transmission Electron Microscopy and Associated Techniques*, Oxford University Press, New York, 1988.