The Effect of Organic Compounds on the Synthesis of Nanophase Materials

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Abstract:

In this study, we investigated the effect of the organic molecules glycine and ethylamine on the synthesis of ZnS nanocrystals. The organic molecules were introduced during a low temperature (180°C) hydrothermal synthesis of ZnS. High resolution transmission electron microscope (HRTEM) images show that the morphology and structure of the ZnS crystals formed in the experiments were affected by the ethylamine, but not by the glycine.

Using ethylamine as the organic molecule, the morphology of the nanocrystals changed from spherical, to lamellar, to rod-like aggregates as the concentration of ethylamine was increased. The crystals were mostly in the stable cubic form. The thermodynamically-unstable hexagonal phase of ZnS was also observed in nanorods and stacking faults within the cubic phase in experiments run with intermediate concentrations of ethylamine.

Introduction:

The study of nanocrystals is important for their future use in possible nanoscale optical or electronic devices. Their unique properties are usually highly dependent on their crystallographic structure. Therefore size and shape are very important factors to consider when trying to synthesize nanocrystals with a specific property. ZnS is a good group II-IV semiconductor, and emits light in the blue part of the spectrum. ZnS is a naturally occurring metal that has two polymorphs at room temperature. The stable cubic sphalerite form and the meta-stable hexagonal wurtzite form. The wurtzite is rarer in nature, as it more unstable by about 13 kJ/mole at room temperature and is only stable at higher temperatures.

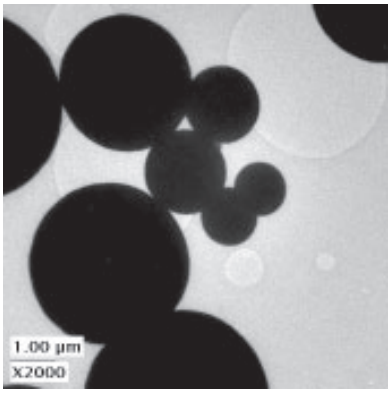

Figure 1: ZnS in sphere morphology synthesized in 0.5M glycine.

The purpose of this research is to determine how organic molecules can affect the shape and morphology of ZnS nanocrystals, using a hydrothermal synthesis method. The crystallographic structure will be characterized using HRTEM imaging.

Procedure:

Synthesis: Thiorea ($SC(NH_2)_2$) was used as the sulfur source in this experiment because it dissolves and releases S^{2-} ions only at higher temperatures. Zinc acetate ($Zn(CH_3COO)_2$) was used as the Zinc source. The samples were prepared with 0.8M and 0.4M of thiorea and zinc acetate, respectively, in water or a solution of water and either ethylamine or glycine with concentrations of organics ranging from 0.5M to 2.0M. These solutions were created in 30 mL - Teflon® cups, sealed, and placed in an autoclave. They were kept at 180ºC for 2 hours, removed and allowed to cool to room temperature naturally. The solutions containing product were then centrifuged, had the supernatant poured off, washed with distilled water, which was repeated ten times to remove impurities in the sample.

Ethylamine was chosen as an organic to use because of its similarity in structure to ethylenediamine, a molecule that has been used previously to synthesize pure wurtzite ZnS [1]. Glycine was chosen because it is the most basic amino acid, and has a similar functional amine group to ethylamine.

Characterization: Samples were characterized using a JEOL 2010 transmission electron microscope (TEM) and a Oxford Energy Dispersion Spectroscopy (EDS) system. Samples were prepared for character-

ization by placing them in an ultrasonic bath for 60 seconds and dispersing the sample from a suspension directly onto holey carbon-coated copper grids.

Results and Conclusions:

Glycine: The TEM images for glycine showed that the organic molecule had little to no effect on the structure and morphology of the ZnS nanocrystals. Figure 1 shows the overall shape of the crystals to be spherical and ranging from 1-5 μm in diameter. As the concentration of glycine in reaction medium increased from 0.5 to 2.0M, general morphology of the crystals remained in this spherical shape. HRTEM revealed that the ZnS was in the cubic sphalerite form.

Some of the crystals observed with about 1.0M glycine were destroyed when placed under the high energy electron beam of the TEM. It is possible that glycine was incorporated into the ZnS crystal structure. When exposed to the high energy of the electron beam, the glycine molecules could be destroyed and the rest of the ZnS structure then appears to fall apart as seen in Figure 2.

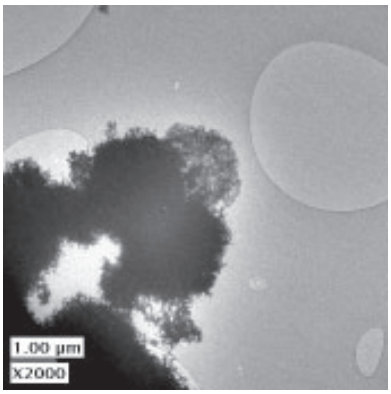

Figure 2: ZnS spheres after being exposed to high energy electron beam.

Ethylamine: Ethylamine had a large influence on the structure of the ZnS crystals. As the concentration of ethylamine in reaction medium increased from 0.5 to 2.0M, there was a wide range of structures seen. Starting at a spherical morphology, the crystals changed to an aggregate of lamellar plates, to nanorods, to clusters of small crystals. HRTEM images of medium concentrations of ethylamine (1.25-1.75M) revealed increasing sections of wurtzite ZnS plates forming as seen in Figure 3. At 1.50M of ethylamine, interesting wurtzite nanorods were observed. These nanorods were growing along an unusual axis of growth. Wurtzite nanorods observed in previous experiments involving ZnS showed growth along the C axis, while these nanorods showed wurtzite growth along the A axis as seen in Figure 4. To our knowledge these structures have not been previously found in synthesis of ZnS nanocrystals.

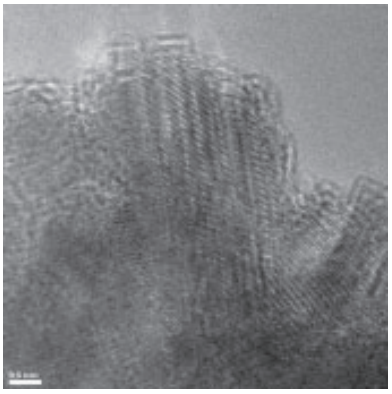

Figure 3: HRTEM image of wurtzite plates forming in 1.25M ethylamine.

Acknowledgements:

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References:

[1] X. Chen, H. Xu, N. Xu, F. Zhao, W. Lin, G. Lin, Y. Fu, Z. Huang, H. Wang, M. Wu, "Kinetically Controlled Synthesis of Wurtzite ZnS Nanorods through Mild Thermolysis of Covalent Organic-Inorganic Network", Inorg. Chem. 2003, Vol. 42, pp. 3100-3106.

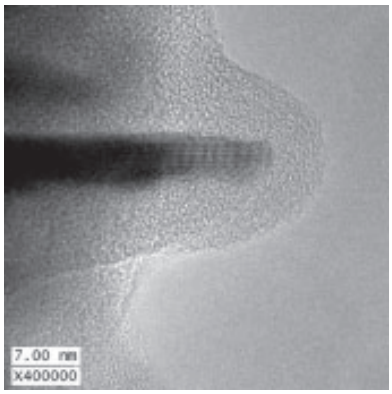

Figure 4: HRTEM image of wurtzite nanorod growing in unusual direction.