

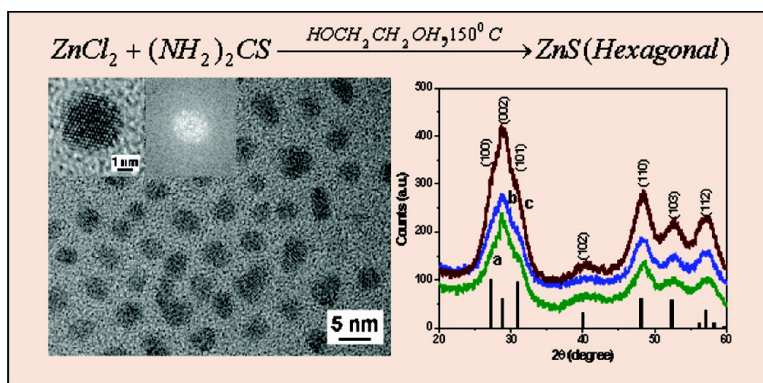
Communication

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Low-Temperature Synthesis of Hexagonal (Wurtzite) ZnS Nanocrystals

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As an important member in the family of wide-gap semiconductors, ZnS has been extensively investigated.¹ ZnS is among the oldest and probably the most important materials used as phosphor host.² By doping ZnS with different metals,³ a variety of luminescent properties excited by UV, X-rays, cathode rays, and electroluminescence have been observed. Owing to its excellent transmission property and its high index of refraction (2.27 at 1 μm), ZnS is also a very attractive candidate for applications in novel photonic crystal devices operating in the region from visible to near-IR.⁴ In the past decade, numerous results⁵ have been reported on the synthesis of nanometer scale semiconductor crystals (quantum dots, nanowires, nanorods, etc.) because their properties, due to quantum confinement effect,⁶ dramatically change and, in most cases, improve as compared with their bulk counterparts.⁷ Among them, ZnS nanocrystals (NCs), again, have been receiving much interest. The structure evolution of ZnS NCs with particle size and their chemical environment have also been the center of research.⁸ Summarizing the results from literature, we found that ZnS NCs mostly synthesized by colloid chemistry usually have the cubic zinc blende (sphalerite) structure^{5f} which is a stable phase at low temperatures for ZnS. Hexagonal (wurtzite) phase is the high-temperature polymorph of sphalerite which can be formed at temperatures higher than 1296 K.^{5e,8a} There were only a few cases^{5e,g,9} where pure wurtzite ZnS NCs were obtained either with high temperature or with solvothermal reaction. One example^{5e} is to thermally decompose the precursor $\text{ZnS}\cdot(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_{0.5}$ formed by solvothermal reaction of Zn^{2+} with thiourea in ethylenediamine medium at 120–180 °C. Even in that case, a minimum temperature of 250 °C is required to obtain wurtzite ZnS nanosheets, not to mention the solvothermal condition required to generate the precursor.

In this Communication, we report a novel and facile low-temperature (150 °C) synthesis of hexagonal ZnS NCs that have an average size less than 5 nm as shown in Figure 1. The synthesis is very simple and yet different from conventional colloid chemistry methods. The method may also be applied to fabrication of other semiconductor NCs. The surprising ability of achieving a high-temperature stable phase at very low temperatures not only provides economically viable route for applications but also opens a new avenue to study structural kinetics and chemistry of semiconductor NCs.

Polyols such as ethylene glycol (EG) have been widely used for synthesizing nanoparticles of transition metals¹⁰ and semiconductors¹¹ assisted by either ultrasonic^{11a} or microwave energy.^{11b} We adopted EG as the reaction medium for synthesizing ZnS NCs. In a typical experiment, 7.34 mmol of anhydrous ZnCl_2 and 14.86 mmol of tetramethylammonium hydroxide (TMAH) are dissolved into 50 mL of EG and heated to 100 °C (solution 1); 7.34 mmol of thiourea is separately dissolved into another 50 mL of EG (solution 2). Under vigorous magnetic stirring, solution 2 is then quickly injected into solution 1. The mixed solution is clear until the solution is heated to 150 °C; then after about 10 min the solution becomes

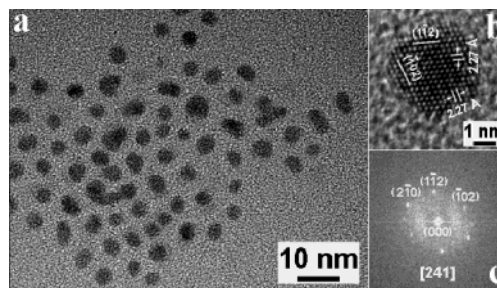


Figure 1. (a) Low magnification TEM graph of as-synthesized ZnS NCs. (b) HRTEM graph showing the lattice fringes pattern of an individual particle. (c) Corresponding FFT image indicating a hexagonal structure.

milky white, indicating the formation of ZnS NCs. At this initial stage, the first aliquot of reaction solution is taken out for characterization of materials at this stage. The remaining solution is then maintained at 150–160 °C for 2 h and the color of reaction solution became milky white mixed with light yellow; a second aliquot of reaction solution is taken out. The rest of the solution is heated further to boiling (~194 °C) and refluxing for another 1 h and used as the third aliquot. All three aliquots are cooled to room temperature (RT), and ZnS nanocrystals are separated from the reaction solution by centrifugation, washed with acetone and ethanol, and finally dried in a desiccator. The dried ZnS powders, which can be redispersed in ethanol for UV/vis spectrum measurements, are used for structural characterization using X-ray diffraction (XRD) and transmission electron microscopy (TEM).

As demonstrated in Figure 1a, the as-synthesized ZnS NCs from the second aliquot are quite uniform in both shape and size. The average size estimated from Figure 1a is 4.2 nm with standard deviation of 0.6 nm. Figure 1b shows an HRTEM graph of an individual particle where lattice fringe pattern illustrates the nanoparticles are well crystallized. The corresponding FFT image (Figure 1c) clearly reveals hexagonal structure. The measured *d*-spacing of (102) planes from the HRTEM graph is 0.23 nm, matching fairly well to the JCPDS No. 80-0007.

XRD patterns are shown in Figure 2 for ZnS nanoparticles from the second aliquot (bottom curve), the third aliquot (middle curve), and the latter sample annealed in Ar atmosphere at 250 °C for 2 h (top curve). The diffraction patterns for all three samples match well to hexagonal ZnS (JCPDS No. 80-0007, vertical bars). The diffraction peaks are significantly broadened because of the very small crystallite size. We cannot exclude the existence of cubic ZnS phase from XRD patterns alone because of the large similarity in the structures between cubic and hexagonal ZnS. However, close inspection of randomly selected individual particles by HRTEM does not seem to reveal any cubic phase. One thing is clear, that the hexagonal ZnS phase is indeed formed at temperature as low as 150 °C under ambient condition. From Figure 2, it is also evident that neither refluxing at 194 °C nor annealing at 250 °C in Ar significantly changes the diffraction pattern, implying that the size of ZnS crystallites does not increase at higher reaction temperature

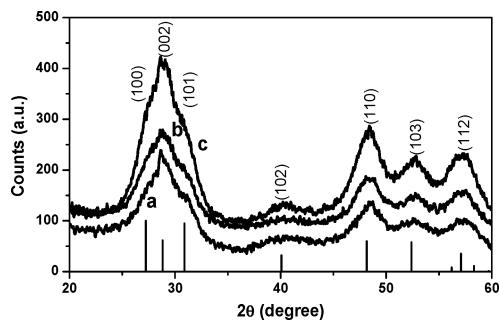


Figure 2. XRD patterns of ZnS NCs obtained at 150–160 °C (a), subsequently refluxing at 194 °C (b), and annealed in Ar at 250 °C (c). Vertical bars indicate standard hexagonal ZnS peak positions from JCPDS No. 80-0007.

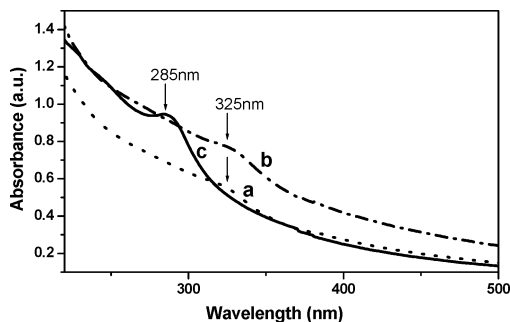


Figure 3. UV/vis spectra of ZnS NCs dispersed in ethyl alcohol: (a) and (b) are for sample obtained at 150–160 °C (dotted line) and subsequently refluxing at 194 °C (dash-dotted line), respectively; (c) is for sample obtained at initial stage (solid line).

and the nanoparticles are well separated. The latter is also evidenced in Figure 1. It should be mentioned that in the synthesis it is essential after the injection of solution 2 into solution 1 that the temperature of the reaction solution to be maintained below 174–177 °C for a certain time, otherwise thiourea decomposes resulting in very low ZnS yield. This is probably also the reason the crystallites do not grow larger after refluxing at 194 °C.

The UV/vis spectra of ZnS nanoparticles dispersed in ethyl alcohol are shown in Figure 3. The spectra for samples from the second aliquot (curve a) and the third aliquot (curve b) are very similar: only a shoulder appears at about 325 nm corresponding to the onset of UV absorption. According to the empirical relationship between the average size of ZnS nanoparticles and the onset of UV absorption given by Banfield et al.,^{8d} we estimate the particle size to be about 4.5 nm, which is in good agreement with TEM observation. This again illustrates that the size of ZnS crystallites does not change after refluxing at 194 °C. Curve c is for the sample from the first aliquot; the absorption peak (285 nm) is strongly blue-shifted, indicating a smaller particle size of about 2.5 nm, again consistent with size (~ 2.9 nm) determined from the small-angle X-ray diffraction data (see Supporting Information).

Finally, to examine whether TMAH induced the formation of hexagonal ZnS NCs at such low temperatures, we performed a similar experiment without TMAH. We still obtained hexagonal

ZnS NCs as evidenced from XRD data (see Supporting Information). The only difference is the product has white color mixed with light pink instead of light yellow. Using other polyols such as diethylene glycol and glycerol without TMAH, we also obtained hexagonal ZnS NCs (see Supporting Information). Therefore, we tend to conclude that polyol plays a key role in forming hexagonal ZnS NCs at low temperatures. Polyol probably forms some intermediates with ZnS such as the one reported in ref 5e which, however, can decomposes into wurtzite ZnS at lower temperatures. The exact mechanism is not known at this moment.

To summarize, we have synthesized close to monodispersed hexagonal ZnS NCs at temperatures as low as 150 °C in a polyol medium. This method should also apply to the synthesis of other II–VI semiconductor NCs such as CdS. We would also like to stress that the work reported here may help to provide a better understanding of the crucial factor determining the crystal structure of nanosized semiconductors.

Supporting Information Available: Small-angle X-ray diffraction data for ZnS NCs obtained from the first aliquot and the XRD data for samples obtained under different conditions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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