

A Solvothermal Elemental Reaction To Produce Nanocrystalline ZnSe

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Introduction

The preparation and characterization of II–VI nanoscale semiconductor compounds have attracted much attention over the past few years due to their great potential in many optoelectronic applications.^{1–4} Now, nanocrystalline ZnS has been widely and deeply investigated^{5,6} since nanosized ZnS can be easily prepared. ZnSe is also an important direct band gap material. Laser diodes based on ZnSe have been successfully demonstrated to operate in a CW mode at room temperature.^{4,7,8} Nevertheless, few reports of the preparation of nanocrystalline selenides could be found generally because a selenium source was not like a sulfur source, which could exist in various stable phases, almost all of which were easily obtainable. Steigerwald has reported a dealkylsilylation method to form CdSe using cadmium alkyl and silyl selenide.⁹ The nanocrystalline ZnSe was mostly prepared by molecular beam epitaxy (MBE),³ metalorganic chemical vapor deposition (MOCVD),⁴ and organometallic vapor phase epitaxy (OMVPE).¹⁰ Almost all of these methods needed a special device, and these methods usually used toxic metalorganic reagents as precursors. We know that the most straightforward way to synthesize the zinc selenide is the direct combination of elemental zinc and selenium at high temperature, but the products from the high-temperature reaction are not nanosized. Rauchfuss^{11–14} has reported a successful fabrication of ZnS and CuS using elemental reactions at reflux in coordinating solvents such as pyridine and *N*-methylimidazole. In addition, Parkin¹⁵ reported a room-temperature liquid ammonia route to prepare metal chalcogenides, but most of his products were amorphous. Recently, we have

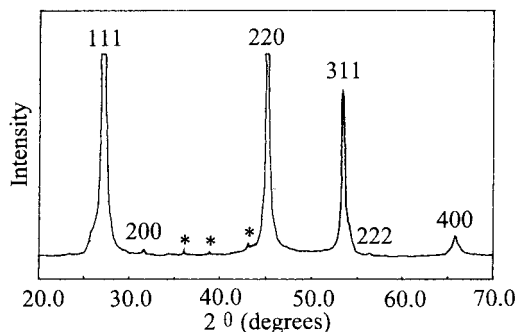


Figure 1. XRD pattern of nanocrystalline ZnSe.

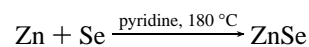
succeeded in preparing the cadmium chalcogenides through a solvothermal synthesis method.¹⁶

In this paper, we report a solvothermal elemental reaction to produce nanocrystalline ZnSe using pyridine as the solvent. The effects of solvent and time are initially investigated. We discovered that the reaction was strongly influenced by the coordinating ability of the solvent. Nanocrystalline ZnS was also synthesized under similar reaction conditions.

Our solvothermal elemental reaction is analogous to the reported method.^{17,18} An appropriate amount of zinc powder (99.99%) and selenium powder (99.95%) were added into a Teflon-lined autoclave of 100 mL capacity. Then the autoclave was filled with pyridine up to 70% of the total volume. The autoclave was sealed into a stainless steel tank and maintained at 180 °C for 8 h without shaking and stirring. After cooling to room temperature naturally, a brown precipitate was obtained. The sample was filtered off, washed with distilled water and absolute ethanol, respectively, and then dried in a vacuum at 80 °C for 3 h.

The sample was characterized by X-ray powder diffraction (XRD) studies, using a Japan Rigaku Dmax rA X-ray diffractometer with graphite-monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Photomicrographs were carried out on a Hitachi model H-800 transmission electron microscope (TEM), using an accelerating voltage of 200 kV.

The formation of nanocrystalline ZnSe results from the combination of metal zinc and selenium by electron transfer. The synthesis reaction can be formulated as follows:



The obtained sample was characterized by the XRD pattern shown in Figure 1. The peaks could be indexed as the cubic

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- (1) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.
- (2) Bawendi, M. G.; Carroll, D. J.; Wilson, W. L.; Brus, L. E. *J. Chem. Phys.* **1992**, *96*, 946.
- (3) Zhang, B. P.; Yasuda, T.; Segawa, Y.; Yaguchi, H.; Onabe, K.; Edamatsu, E.; Itoh, T. *Appl. Phys. Lett.* **1997**, *70* (18), 2413.
- (4) Harris Liao, M. C.; Chang, Y. H.; Chen, Y. F.; Hsu, J. W.; Lin, J. M.; Chou, W. C. *Appl. Phys. Lett.* **1997**, *70* (17), 2256.
- (5) Ohtaki, M.; Oda, K.; Eguchi, K.; Arai, H. *Chem. Commun.* **1996**, 1209.
- (6) Li, Y.; Ding, Y.; Zhang, Y.; Qian, Y. T. Novel Photophysical Properties of ZnS Quantum Dots. Submitted to *Appl. Phys. Lett.*
- (7) Haase, M. A.; Baude, P. F.; Hafedorn, M. S.; Qiu, J.; DePuydt, J. M.; Cheng, H.; Guha, S.; Hoffer, G. E.; Wu, B. *J. Appl. Phys. Lett.* **1993**, *63*, 2315.
- (8) Nakayama, N.; Itoh, S.; Ohata, T.; Nakano, K.; Okuyama, H.; Ozawa, M.; Ishbashi, A.; Ikeda, M.; Mori, Y. *Electron. Lett.* **1993**, *29*, 1488.
- (9) Stuczynski, S. M.; Brennan, J. G.; Steigerwald, M. L. *Inorg. Chem.* **1989**, *28*, 4431.
- (10) Bourret-Courchesne, E. D. *Appl. Phys. Lett.* **1996**, *68* (17), 2418.
- (11) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6385.
- (12) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 2514.
- (13) Paul, P. P.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1993**, *115*, 3316.
- (14) Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043.
- (15) Henshaw, G.; Parkin, I. P.; Shaw, G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 231.

- (16) Li, Y.; Liao, H. W.; Ding, Y.; Fan, Y.; Zhang, Y.; Qian, Y. T. Novel Solvothermal Synthesis of CdE (E = S, Se, Te) Semiconductor Nanorod. Submitted to *J. Am. Chem. Soc.*
- (17) Li, Y.; Duan, X. F.; Qian, Y. T.; Yang, L.; Ji, M. R.; Li, C. W. *J. Am. Chem. Soc.* **1997**, *119*, 7869.
- (18) Li, Y.; Duan, X. F.; Liao, H. W.; Qian, Y. T. *Chem. Mater.* **1998**, *10* (1), 18.

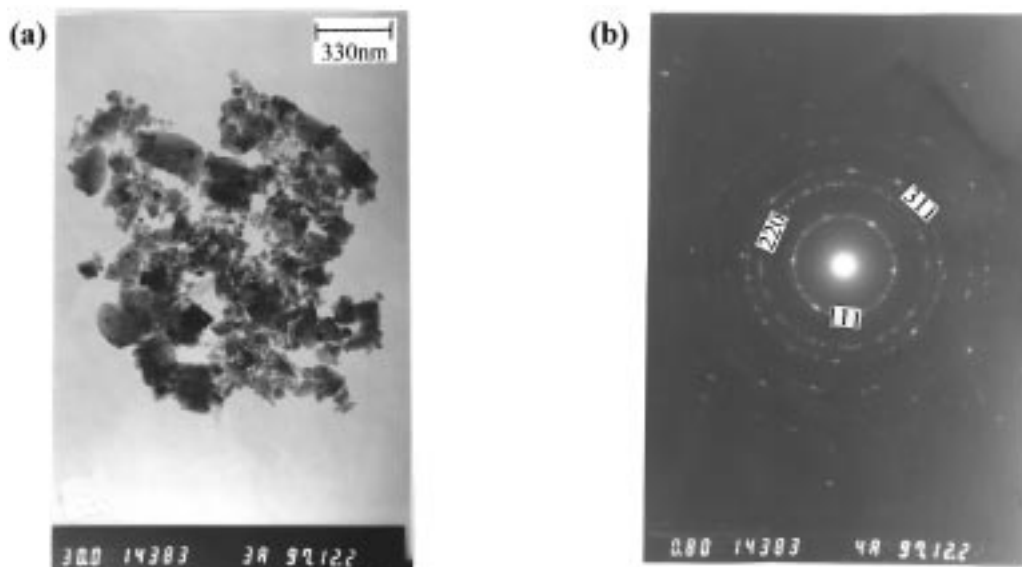


Figure 2. TEM micrographs of nanocrystalline ZnSe.

zinc selenide with a lattice parameter $a = 5.6685 \text{ \AA}$, which was close to the reported data (JCPDS card, No. 37-1463, $a = 5.6688 \text{ \AA}$). The broadening of these diffraction peaks indicated that the sample was nanosized. Estimating from the Debye–Scherrer formula, the average size of the sample was 13.5 nm. There were some other small peaks, marked with asterisks in Figure 1, that could be attributed to a little unreacted zinc powder. No characteristic peaks of other impurity phases were obvious.

TEM micrographs of ZnSe nanocrystalline are given in Figure 2. As shown in Figure 2, the nanocrystalline ZnSe was platelike and spherical. If discriminated carefully, these plates were mostly formed by the aggregation of ZnSe nanoparticles. The size of these particles ranged from 12 to 16 nm, which was generally consistent with the XRD analysis. The electron diffraction pattern also identified that the nanocrystalline ZnSe was cubic blende structure. From the pattern, the reflections of planes 111, 220, 311, 400, 331 and so on were clearly seen.

In order to investigate the influence of different solvents, we substituted pyridine with benzene and ethylenediamine, respectively, and kept the other reaction conditions constant. From the XRD analysis, the reaction in benzene did not produce a selenide, and the product was mostly the unreacted zinc powder. The XRD pattern did not show the existence of selenium because selenium can dissolve in the benzene. However, for the reaction in ethylenediamine, many diffraction peaks appeared in the XRD pattern, but no characteristic peaks of Zn, Se, or ZnSe appeared. We attributed the diffraction peaks to the stable coordination phase which consisted of zinc, selenium, and ethylenediamine. According to the reports of Rauchfuss^{11–14} and Parkin,¹⁵ these low-temperature elemental reactions between metal and chalcogen could be promoted in coordinating alkylamine solvents, such as ammonia and pyridine, since these alkylamine solvents could activate the metal surface by removing the passivating surface oxide coating. This is why the reaction in benzene did not show the zinc selenide phase. In contrast, ethylenediamine is such a strong coordinating solvent that the zinc selenide also cannot be formed through the conversion of the stable zinc coordination compound produced under these reaction conditions.

We also successfully synthesized nanocrystalline ZnS through this solvothermal elemental reaction in pyridine. We found that the reaction time and temperature played an important role in the particle size of the product. When the reaction time was 5 h,

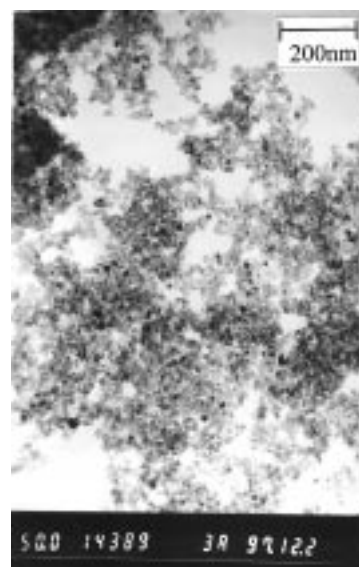


Figure 3. TEM micrograph of nanocrystalline ZnS (at 180 °C for 10 h).

the size of the ZnS produced was about 3 nm estimated from the X-ray line broadening. The size was about 10 nm when the time was 10 h and no less than 18 nm for 24 h. These results were all supported by the TEM images. From Figure 3 (reaction time 10 h), we could see that the nanocrystalline ZnS was also spherical and well dispersed.

In summary, we have succeeded in synthesizing nanocrystalline ZnSe and ZnS, using a relatively simple solvothermal elemental reaction method. The coordinating ability of the solvent could strongly influence the reaction process, and the particle size of the product increased with an increase in reaction time. This method can be easily controlled and is expected to be applicable to fabricate other nanosized semiconductor compounds.

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