

# Preparation of ZnS nanoparticles by ultrasonic radiation method

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**Abstract.** Zn nanoparticles were prepared by the inert-gas evaporation technique with induction heating method. As-prepared Zn particles were mixed with Na<sub>2</sub>S solution. ZnS nanoparticles were synthesized under ultrasonic radiation. They were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), UV spectrophotometry, and X-ray photoelectron spectrometry (XPS). XRD revealed that the ZnS nanoparticles prepared have a zincblende structure. TEM observations showed that the ZnS nanoparticles are in a spherical form with an average diameter of 40 nm. XPS results proved that, for our sample, the binding energies of Zn 2*p* and S 2*p* are the same as those of bulk single-crystal, but the full widths at half maximum of the XPS peaks are larger than those of bulk single-crystal.

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Semiconductor nanoparticles have various properties, that differ from those of corresponding bulk materials partly because of the three-dimensional confinement of electrons and holes in a small volume or the fact that the number of atoms on the surface is comparable to that inside the particles [1–5]. The surface of a nanoparticle is more important than the bulk as regards its properties, as nanoparticles have larger surface-to-volume ratios. Surface atoms are bound by weaker forces because of missing neighbors, which leads to high surface reactivity. The surface is the stage on which sublimation, desorption, adsorption, chemical reaction, etc. occur. There has been considerable interest in preparing semiconductor nanoparticles [6–9]. They can be prepared in the form of dispersed colloids [10] or trapped and stabilized within micelles [11], polymers [12], zeolites [13], or glass [14]. In most cases, particles prepared by these methods have poorly defined exterior surfaces and a relatively broad size distribution. The sol–gel technique is one of the most common methods for preparing semiconductor nanoparticles. During this process, a stabilizing agent is usually added in order to protect the particles from growth. The stabilizing agent formed on the

surface of semiconductor particles may strongly change the character of semiconductor particles. How to prepare semiconductor nanoparticles with clean surfaces is also an important issue.

ZnS nanoparticles have the potential for applications in areas such as nonlinear optical devices and fast optical switches, and have been studied extensively. Because most reported ZnS nanoparticles are prepared and stabilized by capping or passivation with organic materials, the influence of the stabilizer on ZnS nanoparticles could not be avoided. In this paper, we present a new method for preparing ZnS nanoparticles without any stabilizer, which makes it possible for us to study the real properties, especially the surface character, of ZnS nanoparticles. First, Zn nanoparticles were prepared by the inert-gas evaporation technique with induction heating. These Zn nanoparticles were mixed with Na<sub>2</sub>S solution under ultrasonic radiation. Normally, Zn can not react chemically with Na<sub>2</sub>S effectively. However, in the nanometer range, this reaction may occur as Zn nanoparticles have high surface reactivity. After chemical reaction, the product was washed with distilled water and dried under reduced pressure. The sample was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectrometry (XPS). By using a UV spectrophotometer, the optical absorbance was also examined.

## 1 Experiments

### 1.1 Preparation of Zn nanoparticles

Zn nanoparticles were prepared by the inert-gas evaporation technique with induction heating method. As is well known, when a metal is put in a varying magnetic field, there exists an induction current in the metal which can heat up the metal itself. When the induction current is increased to a given value, metallic Zn atoms are emitted from the thermal source. As a result of interatomic collisions with gas atoms, the evaporated Zn atoms lose kinetic energy and condense on a vertical cold finger. When the sample is taken out from the evaporation chamber, an oxide layer must form on the surface of a Zn

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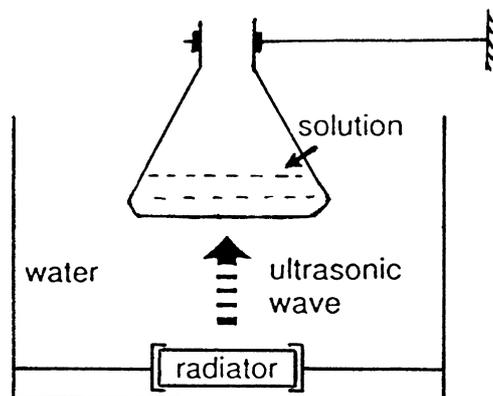
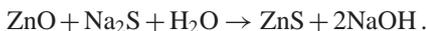
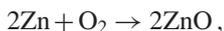


Fig. 1. A schematic diagram of the ultrasonic device

particle. This can be proved by XRD and XPS techniques. From TEM observation, the average particle size can be estimated to be about 80 nm. In the following, the sample is referred to as Zn/ZnO.

### 1.2 Preparation of ZnS nanoparticles

In our study, ZnS nanoparticles were prepared in a Na<sub>2</sub>S solution–Zn/ZnO suspension system under ultrasonic radiation. Figure 1 shows a schematic diagram of the ultrasonic radiation device. Preparation of ZnS nanoparticles in the present system may proceed as follows:



First, sodium sulfide was dissolved in distilled water. The concentration of the solution was 0.2 mol/l. An appropriate amount of Zn/ZnO nanoparticles was added into the solution. During the reaction, the solution was radiated by an ultrasonic device and the solution temperature was kept at 50 °C. After a given reaction time of 20 h, the sample was washed many times with distilled water using ultrasonic agitation and centrifuging. Finally, the sample was dried at 50 °C under reduced pressure for 5 h.

The X-ray diffraction (XRD) spectrum of the specimen was obtained by using CuK<sub>α1</sub> ( $\lambda = 0.15405$  nm) irradiation on a Regaku D/Max- $\gamma$ C X-ray spectrometer. The size and morphology of the particles were determined by a JEM-200CX transmission electron microscope (TEM). The UV-VIS absorption spectra were measured using a Hitachi 340 spectrophotometer. A photoelectron spectrometer employing Al K<sub>α</sub> X-rays was employed to examine the chemical states of the surface atoms.

## 2 Results

The X-ray diffraction spectrum of the as-prepared sample is shown in Fig. 2. The diffraction peaks located at  $2\theta = 28.57^\circ$ ,  $33.19^\circ$ ,  $47.63^\circ$ ,  $56.49^\circ$ , and  $76.95^\circ$ , coincide with those of  $\beta$ -ZnS [111], [200], [220], [311], and [331], respectively. Their intensity ratio is 100:11:71:39:13, which is in agreement with that of  $\beta$ -ZnS single-crystal. This means that ZnS

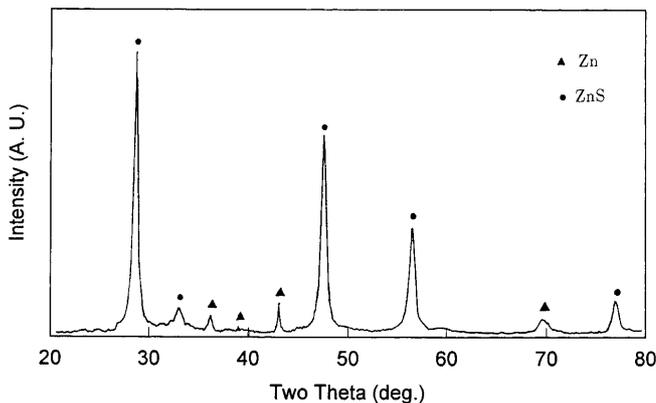


Fig. 2. X-ray diffraction spectrum of as-prepared sample

crystallites prepared in this study have a zincblende structure. However, we also find four diffraction peaks corresponding to metallic zinc, which comes from the raw materials.

In general, nanoscale semiconductor particles prepared by wet chemistry tend to precipitate with a glassy structure [15, 16], as opposed to the crystalline state observed in the present work. Actually, even if the size of ZnS particles prepared by this method decreases to a few nanometers, they also have crystalline structure. That may be why we may have observed, for the first time, some interesting results in ZnS nanoparticles, e.g., surface phonon mode [17], nonlinear refraction [18], and photoluminescence.

The particle size and morphology of the sample were investigated by TEM. A TEM micrograph of the sample, as displayed in Fig. 3, shows that the ZnS sample consists of spherical particles with a narrow size distribution, and the average diameter of the particles is about 40 nm. Figure 4 shows the UV-VIS spectrum of the ZnS nanoparticles. The spectrum of bulk ZnS is also shown in Fig. 4 for compar-

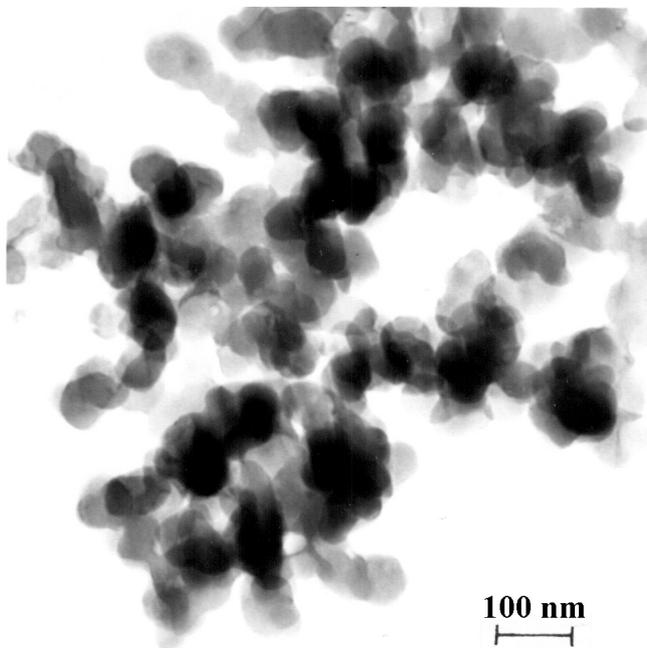


Fig. 3. TEM micrograph of the sample

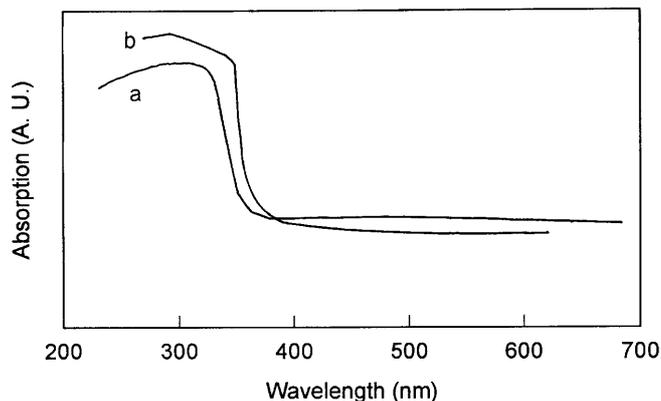


Fig. 4. Optical absorption spectra of the (a) ZnS nanoparticles and (b) bulk ZnS

ison. One can see that the optical absorption edge exhibits a blueshift with respect to that of bulk ZnS. The blueshifts with the decrease in the crystallite size should be attributed to the quantum size effects. The size quantization of carriers in a small volume crystallite is well known to cause the blueshift.

Using an X-ray photoelectron spectrometer, the states of atoms on the surface of the particles were analyzed. The XPS spectra of the S 2*p* and Zn 2*p* were obtained as shown in Fig. 5. For comparison, a bulk  $\beta$ -ZnS single crystal was also measured under the same conditions. Experimental results are listed in Table 1. One can see from Table 1 that the binding energies of surface atoms for the ZnS sample are the same as those for bulk single-crystal. This means the work function, i.e., the energy needed to remove electrons from the

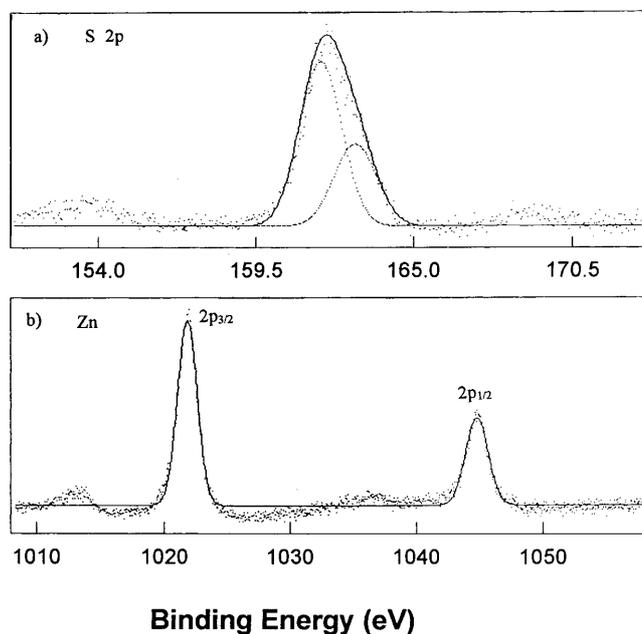


Fig. 5a,b. XPS spectra of a S 2*p* and b Zn 2*p*

Table 1. XPS data obtained from the ZnS nanoparticles sample and the ZnS single-crystal

Level	Binding energy / eV		FWHM / eV	
	sample	single-crystal	sample	single-crystal
Zn 2 <i>p</i> <sub>3/2</sub>	1021.9	1021.9	1.84	1.68
Zn 2 <i>p</i> <sub>1/2</sub>	1045.1	1045.0	2.13	2.11
Zn 3 <i>d</i>	10.6	10.5	1.53	1.38
S 2 <i>p</i> <sub>3/2</sub>	161.9	161.9	1.75	1.42
S 2 <i>p</i> <sub>1/2</sub>	163.2	163.2	1.75	1.40

energy levels, is identical for our sample and single-crystal ZnS. However, the full width at half maximum (FWHM) of the peaks for our sample is always wider than that of single-crystal, which reflects the fact that the surrounding conditions around every atom in our sample are not uniform. Detailed research is in process.

### 3 Conclusions

A new ultrasonic irradiation method to prepare ZnS nanoparticles has been described. The ZnS nanoparticles have been characterized by means of XRD, TEM, UV spectrophotometry, and XPS. Ultrasonic radiation is a dynamic method that does not affect the nature of the particle, and thus is different from surfactant techniques. This approach may be applicable to other materials.

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