

DEVELOPMENT OF A HYDROTHERMAL METHOD TO SYNTHESIZE SPHERICAL ZNSE NANOPARTICLES: APPROPRIATE TEMPLATES FOR HOLLOW NANOSTRUCTURES

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ABSTRACT. Hydrothermal method was used to synthesize pure ZnSe nanosphere materials. The effects of the reducing agent amount, the reaction time and temperature were investigated on the purity of ZnSe. Also, the effects of surfactants such as sodium dodecyl sulfate (SDS) (anionic) and cetyl trimethylammonium bromide (CTAB) (cationic) were studied on the morphology of ZnSe. The prepared nanospheres were characterized using XRD, SEM, TEM and UV-Vis spectroscopy. Through these techniques, it was found that the pure ZnSe nanoparticles have a zinc blend structure and in a spherical form with average diameter of 30 nm.

KEY WORDS: ZnSe, Nanosphere, Hydrothermal, Surfactant

INTRODUCTION

In recent years, synthesis of nanostructured materials has attracted the attention of a large number of research groups. Also, these materials have been widely studied for their unique physical and chemical properties. The preparation of nanomaterials with controlled size, morphologies and size distribution is always potentially important in the synthesis of materials suitable for optoelectronic and luminescent applications [1-3].

As one of the most important II-VI group semiconductors, ZnSe with a room temperature bulk band gap of 2.7 eV, is a good candidate for short wavelength lasers and other optoelectronic devices such as blue-green laser diodes and turnable mid-IR laser sources [4-8].

Size, dimensionality and size distribution are known to play important roles in determining the physical and chemical properties of nanostructured materials [9, 10]. It is difficult to control the size distribution and these results in a broad and profoundly red shifted photoluminescence emission. Hence, there is a need for developing a new approach to obtain monodispersed ZnSe nanoparticles [11].

Various methods such as molecular beam epitaxy, metalorganic chemical vapor deposition and organometallic vapor phase epitaxy have been used to synthesize ZnSe nanoparticles [2, 6, 12]. Solvothermal methods have also been developed for the synthesis of ZnSe and CdSe. The advantage of the solvothermal processes is that they required relatively low temperatures and pressures. However, organic solvents are usually harmful to the environment; therefore the non-toxic solvents would be used for achieve the products in a large scale. Recently, ZnSe nanostructure has been synthesized by using different hydrothermal methods [12].

This work aimed to synthesize ZnSe nanoparticles suitable as templates for fabricating hollow nanostructures. These materials can have a wonderful application in drug delivery and catalysis. In this work, we have reported the effects of the amount of reducing agent, the reaction time and temperature and the type of the surfactant for the preparation of pure ZnSe nanospheres by hydrothermal method.

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EXPERIMENTAL

All the reagents were analytical grade and purchased from Merck Company. Reagents were used without any further purification. In order to obtain a pure phase of monodispersed ZnSe nanospherical particles the synthesis conditions such as: the reducing agent amount, type of the surfactant, the reaction temperature and time have been optimized. The optimization conditions are reported in the following sections. It is noteworthy the Zn to Se molar ratio has been set to be 1 in all experiments.

Synthesis of ZnSe nanosphere particles

Optimization of the reaction temperature. 5 mmol ZnCl₂ (98%), 5 mmol Na₂SeO₃·5H₂O (97%) and 10 mL N₂H₄·H₂O (80%) (Na₂SeO₃·5H₂O to N₂H₄·H₂O molar ratio was equal to 0.025) were sequentially added to 40 mL deionized water under sonication for 3 h using an ultrasound cleaner (VGT-1860QTD, 42 kHz, 150 W). The mixture was transferred into an autoclave, sealed and in different experiments was kept at 80, 100, 130, 150 and 160 °C, respectively, for 8 h. After cooling the system to room temperature, the product was separated by centrifugation, washed with absolute ethanol and deionized water several times, and then dried under vacuum at 60 °C for 10 h.

Optimization of the amount of hydrazine hydrate. The process was the same as in the previous section, using 5 mmol ZnCl₂, 5 mmol Na₂SeO₃·5H₂O and N₂H₄·H₂O, which in different experiments Na₂SeO₃·5H₂O to hydrazine hydrate molar ratio was chosen to be equal to 0.025 (10 mL), 0.05 (5 mL) and 0.0625 (4 mL), respectively. The reaction temperature and reaction time in the autoclave were 160 °C and 8 h, respectively.

Optimization of the reaction time. In order to find the optimum time, the reaction in previous section was carried on at 160 °C for 2, 4, 6, 7 and 8 h. Since the time required for the reaction was found to be 8 h, to prevent repeating, we have reported only the reaction times of 7 and 8 h durations in the following sections.

Synthesis of ZnSe nanospheres with SDS and CTAB surfactants

In a typical synthesis, 5 mmol ZnCl₂ was added to 20 mL of deionized water and sonicated for 15 min. Then solution of surfactants with ZnCl₂ to SDS or CTAB ratio equal to 1 prepared in 20 mL of deionized water and was added slowly to ZnCl₂ solution under sonication. Then, 5 mmol Na₂SeO₃·5H₂O and 5 mL N₂H₄·H₂O (80%) were added and sonicated for 3 h. The mixture was transferred into an autoclave, sealed and kept at 160 °C for 8 h. After cooling the system to room temperature, the product was separated by centrifugation, washed with absolute ethanol and deionized water for several times, and then dried under vacuum at 60 °C for 10 h.

Characterization

Having been purified, the crystal phase and particle size of the synthesized products were characterized by X-ray diffraction (XRD) using FK60-04 with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), and with instrumental setting of 35 kV and 20 mA. The morphology of the nanostructures was observed by emission scanning electron microscopy (SEM, Philips-XL ϕ 30) and transmission electron microscopy (TEM, Philips-CM120). UV-Vis spectra of the ZnSe nanosphere were recorded by MPC-2200, UV2550 UV-Vis spectrophotometer in the wavelength range of 300 to 600 nm. Accessories used in this type of UV-Vis analysis are opal glass and an integrating sphere. The opal glass method involves the placement of a scattering board behind the sample,

resulting in the equalization of scattering coefficients of the reference side and sample side. The integrating sphere method involves a barium sulfate-coated sphere that draws the scattered light, allowing all the light to reach the detector. Since light cannot penetrate opaque samples, it is reflected on the surface of the samples.

RESULTS AND DISCUSSION

In this work, hydrazine hydrate was used as reducing agent. The XRD patterns of ZnSe nanoparticles prepared at various temperatures are shown in Figure 1. During the experiments it was found that when the reaction is running for 8 h at less than 100 °C the ZnSe is not produced and the products are ZnO and black powder of Se. Figure 1a shows the XRD patterns of the obtained products at 80 °C. In these patterns all the diffraction peaks can be well indexed to Se and ZnO phases (JCPDS, No. 38-0768 and 36-1451, respectively). This means that hydrazine hydrate is not acting as a reductant for reducing the SeO_3^{2-} to Se^{2-} at 80 °C and in this condition the hydrazine hydrate has reduced SeO_3^{2-} to Se according to the reaction 1.



A weak new peak is appeared at diffraction degree about 27.28° when the temperature increased to 100 °C (Figure 1b). It may be due to the presence of ZnSe phase in the product. This means that the reduction of SeO_3^{2-} to Se^{2-} ions by the hydrazine hydrate has been started at 100 °C. When the temperature increased to 110-150 °C, Se, ZnO and ZnSe were obtained as reaction products (Figures 1c and 1d). In these conditions three clear peaks are appeared at diffraction degrees 27.28°, 45.23° and 53.58°, which can be well indexed to cubic zinc blend ZnSe (JCPDS, No. 37-1463).

The pure ZnSe nanoparticles can be obtained only when the temperature is above 150 °C. Figure 1e shows the XRD pattern of the pure ZnSe nanoparticles at 160 °C. No other crystalline phase was found in the XRD pattern. Therefore it can be concluded that the pure ZnSe nanoparticles can be synthesized only when the temperature is over 150 °C.

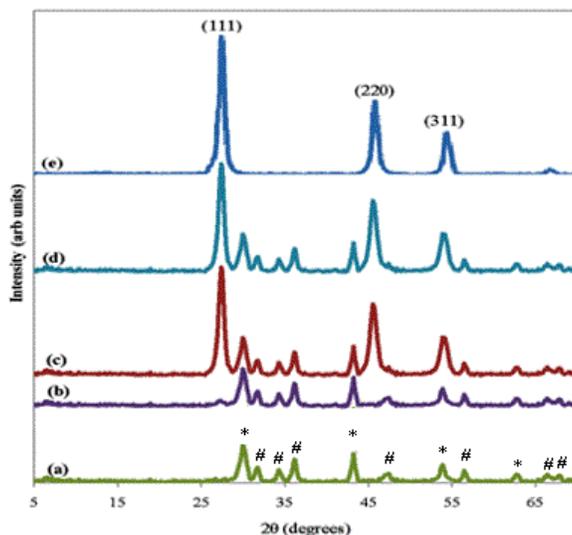


Figure 1. XRD patterns of the prepared samples at the temperatures of: (a) 80 (ZnO = #, Se = *), (b) 100, (c) 130, (d) 150 and (e) 160 °C.

Decreasing of hydrazine hydrate (80%) from 10 to 5 mL had no effects on the purity of the ZnSe phase (Figure 2a). Whereas, when using less than 5 mL of hydrazine hydrate, at 160 °C for 8 h, Se and ZnO phases were reappeared (Figure 2). The results showed that it is required to use 5 mmol of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ (97%) as starting material at least 5 mL of hydrazine hydrate (80%) in order to prepare pure ZnSe at 160 °C for 8 h.

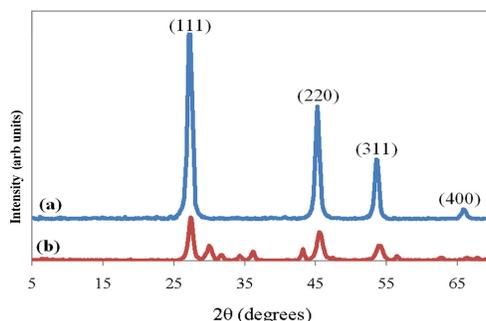


Figure 2. XRD patterns of the prepared ZnSe with: (a) 5 mL and (b) 4 mL hydrazine hydrate.

In order to find the optimum time, the reaction was carried on at 160 °C for 2, 4, 6, 7 and 8 h. Since the time required for the reaction was found to be 8 h, to prevent repeating, here we are reporting only the reaction time of 7 and 8 h durations. Figure 3 shows the XRD pattern of the prepared ZnSe with 5 mL hydrazine hydrates at 160 °C for 7 h. It can be seen that ZnO and Se particles have been appeared again after decreasing the reaction time from 8 to 7 h. Therefore, the pure ZnSe nanoparticles can be obtained only when the temperature is above 150 °C and the reaction duration is 8 h, while the hydrazine hydrate to $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ molar ratio is equal to 0.05.

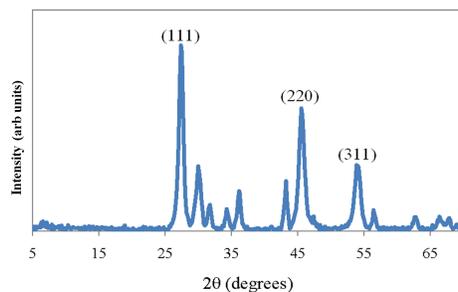


Figure 3. XRD pattern of the prepared ZnSe for 7 h.

The XRD patterns of pure ZnSe nanoparticles prepared with and without surfactant in optimum conditions are shown in Figure 4. All peaks can be well indexed to cubic zinc blend. No other crystalline phase was found in the XRD pattern. Figure 4a shows the XRD pattern of the ZnSe nanospheres prepared without the surfactant. The lattice constant obtained from XRD data was $a = 5.669 \text{ \AA}$, which is consistent with that of the bulk cubic ZnSe (JCPDS, No. 37-1463 Card, $a = 5.66882(8) \text{ \AA}$). Figures 4b and 4c show the XRD patterns of the ZnSe nanospheres prepared with SDS and CTAB surfactants, respectively. In these patterns all diffraction peaks can be indexed to cubic zinc blend (JCPDS, No. 05-0522, $a = 5.667 \text{ \AA}$). The lattice constant of the ZnSe nanospheres prepared with SDS and CTAB surfactants was calculated using XRD data and were 5.663 and 5.649 \AA , respectively (standard deviation =

0.01). These results indicate that the lattice parameter of the nanoparticles are smaller than those of the bulk crystalline ZnSe ($a = 5.667 \text{ \AA}$). It is shown that in most reported nanoparticles, the lattice constants often decrease with decreasing the particle size [12-14]. The different synthesis conditions with products are listed in Table 1.

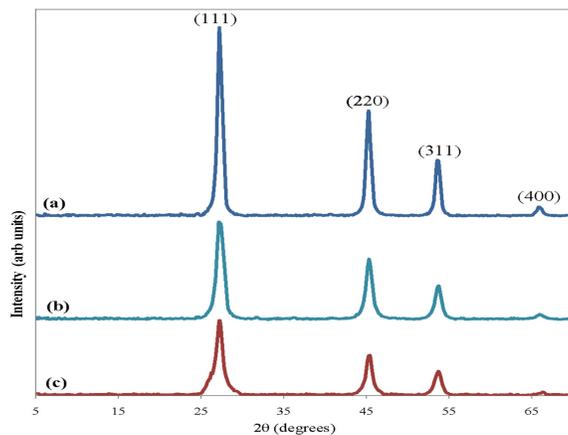


Figure 4. XRD patterns of pure ZnSe prepared: (a) without surfactant, (b) with SDS surfactant and (c) with CTAB surfactant.

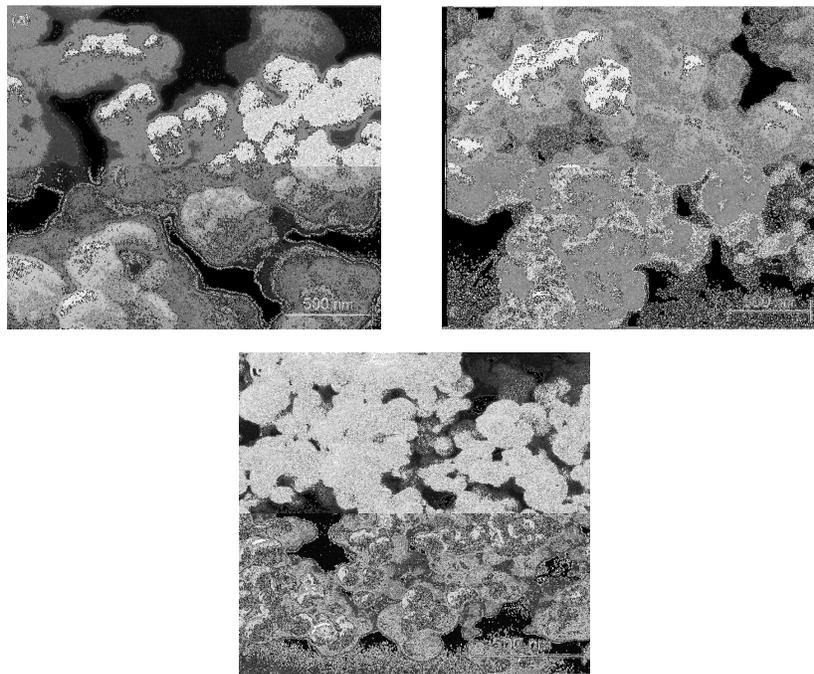


Figure 5. SEM images of ZnSe nanospheres prepared: (a) without surfactant, (b) with SDS surfactant and (c) with CTAB surfactant.

The morphology of the products was observed by SEM and TEM images. The SEM images of the synthesized products are shown in Figures 5(a-c). These images clearly demonstrate that the products are spherical. It can also be seen that there is a well size distribution in all products. The grain size distribution of ZnSe prepared with Zn/Se = 1 is narrow and is consistent with the unimodal normal distribution [15]. This narrowness may also be due to the effect of sonication before transferring into autoclave. The SEM observations show that the samples prepared with surfactants are less aggregated. This can be due to coating of inorganic core by the surfactant, which prevents the nanoparticles to aggregate. It is proved that the prevention of aggregation of nanoparticles in the presence of the surfactant is more effective when the surfactant has a long and branched chain structure [9, 16]. The SEM images show that the ZnSe prepared with CTAB surfactant is less aggregated because of its longer and branched chain structure. The energy dispersive X-ray (EDAX) analyses of prepared samples confirm that the Zn and Se elemental ratio is 1:1 for all ZnSe samples (Figure 6).

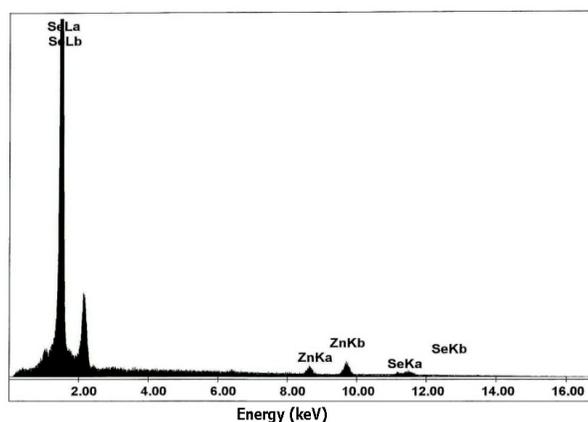


Figure 6. EDX spectrum of ZnSe nanospheres.

The TEM images of the synthesized products are shown in Figures 7(a-c). It is clear that the prepared ZnSe nanoparticles using CTAB surfactant are spherical with average diameter of 30 nm. So far, ZnSe nanostructures with different morphologies have been synthesized. In 2008, Yang *et al.* [18] prepared flower-like ZnSe microstructure and Shi *et al.* [9] synthesized ZnSe nanodonuts by hydrothermal method. ZnSe quantum dots were synthesized by Jiao *et al.* [7] and Jana *et al.* [3] using hydrothermal and solvothermal methods, respectively. These samples are not appropriate templates for hollow nanostructures used in drug delivery. Quantum dots have smaller size than those of most drugs. The other morphologies cannot create uniform spherical hollow structures. In this work, we have prepared a pure sample of nanosphere ZnSe. The nanoparticles with these characteristics are appropriate templates for hollow nanostructures and these hollow nanostructures will show a wonderful application in drug delivery and catalysis. The optical properties of the semiconductor nanomaterials depend on the size and the shape of the particles. UV-Vis spectra of ZnSe samples are shown in Figure 8. The optical absorption spectrum can be used to estimate the bandgap of the semiconductors. The band gap for the prepared ZnSe samples was calculated to be 2.95 and 2.75 eV, with and without surfactant, respectively. The band gap values are obtained by following equation: $E = hc/\lambda$, where λ is estimated from shoulder or peak of the spectra correspond to the fundamental absorption edges in the samples, h is Planck constant, c is the speed of light and E is energy ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$).

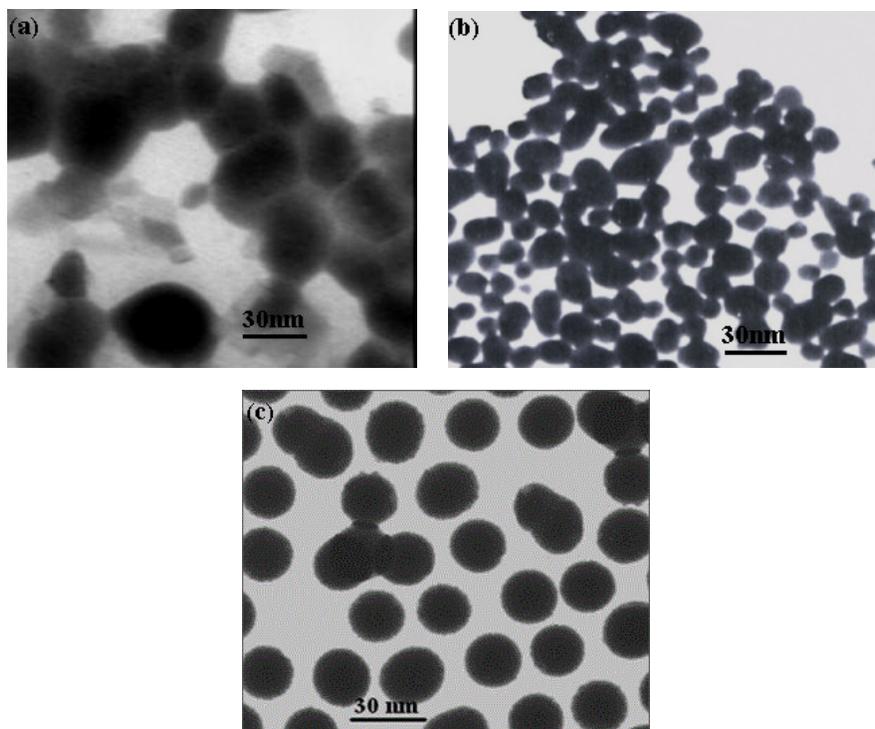


Figure 7. TEM image of prepared ZnSe nanospheres using CTAB surfactant.

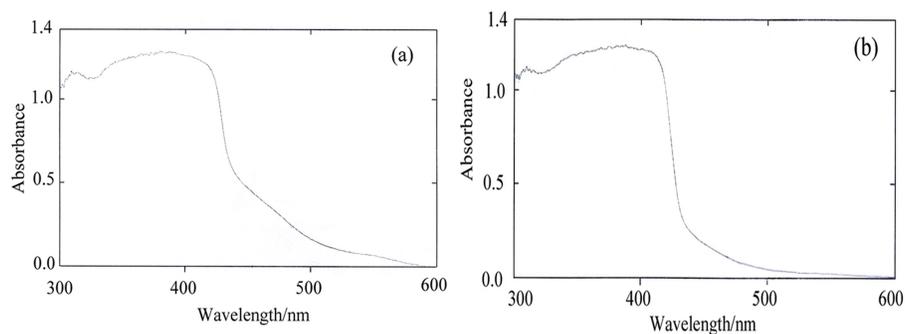


Figure 8. The UV-Vis spectra of ZnSe prepared: (a) without and (b) with CTAB surfactant.

The absorption edge shows a blue shift to higher energies as compared with the bulk ZnSe (2.7 eV). This is due to the fact that smaller particles have larger band gaps and absorb at shorter wavelengths [10, 17, 18]. Investigation of the spectra reveals that the synthesized ZnSe using CTAB surfactant (Figure 8b) has a sharper absorption edge. This is consistent with the SEM images and indicates that the synthesized particles can be considered to be monodispersed.

CONCLUSIONS

ZnSe spherical nanoparticles have been synthesized using hydrothermal method. The results exhibited that the ZnSe nanospheres prepared using CTAB surfactant are spherical and can be considered as monodispersed particles. The nanoparticles with monodispersed nanosphere characteristics are appropriate templates for hollow nanostructures. Therefore, these hollow nanostructures via removal of ZnSe attract the attention of many researchers in applying them in drug delivery and catalysis.

Table 1. Different synthesis conditions with products.

Samples	Sources of Zn and Se	Type of surfactant	Amount of reducing agent	Reaction temperature	Reaction time (h)	products
1	ZnCl ₂ , Na ₂ SeO ₃	-	10 mL	80 °C	8	Se, ZnO
2	ZnCl ₂ , Na ₂ SeO ₃	-	10 mL	100 °C	8	Se, ZnO.ZnSe
3	ZnCl ₂ , Na ₂ SeO ₃	-	10 mL	130 °C	8	ZnSe, Se, ZnO
4	ZnCl ₂ , Na ₂ SeO ₃	-	10 mL	150 °C	8	ZnSe, Se, ZnO
5	ZnCl ₂ , Na ₂ SeO ₃	-	10 mL	160 °C	8	Pure ZnSe
6	ZnCl ₂ , Na ₂ SeO ₃	-	5 mL	160 °C	8	Pure ZnSe
7	ZnCl ₂ , Na ₂ SeO ₃	-	4 mL	160 °C	8	ZnSe, Se, ZnO
8	ZnCl ₂ , Na ₂ SeO ₃	-	5 mL	160 °C	7	ZnSe, Se, ZnO
9	ZnCl ₂ , Na ₂ SeO ₃	SDS	5 mL	160 °C	8	Pure ZnSe
10	ZnCl ₂ , Na ₂ SeO ₃	CTAB	5 mL	160 °C	8	Pure ZnSe

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