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General Sonochemical Method for the Preparation of Nanophasic Selenides: Synthesis of ZnSe Nanoparticles

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ZnSe nanoparticles of about 3 nm in size have been prepared by the sonochemical irradiation of an aqueous solution of selenourea and zinc acetate under argon. The ZnSe nanoparticles were characterized using techniques such as transmission electron microscopy, X-ray diffraction, absorption spectroscopy, differential scanning calorimetry, transmission and diffuse reflection spectroscopy, photoluminescence spectroscopy, and energy-dispersive X-ray analysis. The mechanism of the sonochemical irradiation is discussed. This sonochemical method was found to be a general method for the preparation of other selenides as well.

1. Introduction

Recently, nanoparticles have been the subject of considerable interest in many different scientific disciplines. This interest is the result of the many special properties of materials in the nanoscale regime, such as a large surface-to-volume ratio and the increased surface activity as compared to that of the bulk material. This enables their use in catalysis, as well as mechanical, electric, and optical applications.[1−5] Semiconductor nanoparticles, in particular, exhibit variable and controllable properties, especially, the change of energy structure and enhanced surface properties with a decrease in size that affects their optoelectronic properties.[5] Nanoparticles can be prepared by a variety of methods, such as molecular beam epitaxy,[6] chemical vapor deposition,[7] reduction by ionizing radiation,[8] thermal decomposition in organic solvents,[9] chemical reduction or photoreduction in reverse micelles,[10] and chemical reduction with[11] or without stabilizing polymers.[12] From all of this work, it has been assessed that the colloidal stability (for colloidal solutions), particle size, and properties of nanoparticles depend strongly on the specific method of preparation and the experimental conditions applied.

Currently, the sonochemical method has been used extensively to generate novel materials with unusual properties,[13] because the method causes the formation of particles of a much smaller size and higher surface area than those reported by other methods. The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth, and implosive collapse of bubbles in a liquid. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hotspots have been experimentally determined, with transient temperatures of ~5000 K, pressures of 1800 atm,[14] and cooling rates in excess of 10^{10} K/s. These extreme conditions attained during bubble collapse have been exploited to decompose the metal−carbonyl bonds and generate metals,[14−17] metal carbides,[18] and metal oxides.[19,20]

Selenides, which are very useful materials, have been widely used as thermoelectric cooling materials, optical filters, optical recording materials, solar cells, supersonic materials, and sensor and laser materials.[21−24] Extensive attention has been paid to the preparation and characterization of selenides, owing to their interesting properties and potential applications.

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Traditionally, selenides have been synthesized by solid-state reactions and self-propagating high-temperature synthesis that require high temperatures for initiation of the reaction.[25−26] There are some reports about ZnSe synthesis via chemical bath deposition,[27−31] molecular beam epitaxy,[32] organometallic vapor phase[33] and direct combination of elemental zinc and selenium in an autoclave in the presence of pyridine.[34]

In the present paper, we report a novel sonochemical method for the preparation of ZnSe semiconductor nanoparticles that are widely used due to their role in the photoluminescence, electroluminesce devices, and *n*-type window layers for thin-film heterojunction solar cells.[35−38] This method is proposed as a general method for the preparation of selenides. It has been also employed for the preparation of CuSe and PbSe.

ZnSe nanoparticles were prepared by the ultrasonic irradiation of an aqueous solution of selenourea and zinc acetate under an argon atmosphere. These nanoparticles are approximately 3 nm in size, as calculated using the Debye−Scherer formula.[39] The ZnSe nanoparticles are also characterized using powder X-ray diffraction (XRD), UV−vis spectroscopy, transmission and diffuse reflection spectroscopy (DRS), photoluminescence spectroscopy (PL), energy-dispersive X-ray analysis (EDAX), and transmission electron microscopy (TEM).

2. Experimental Section

1. Materials. Selenourea (99.9%) and $Zn(Ac)_2$ (99%) were purchased from Aldrich and used without further purification. Doubly distilled water was used. The absolute ethanol used was from Pharmco Products. Ultrasonic irradiation was accomplished with a high-intensity ultrasonic probe (Misonix, XL Sonifier, 1.13 cm diameter; Ti horn, 20 Hz, 60 W cm^{-2}).

2. Instruments. The instruments used in this report for TEM, EDAX, and DSC measurements have been described elsewhere.[19,20] The instruments that were employed for other measurements will be describe herein. (i) Absorption spectra were recorded on a Hewlett-Packard 8453 UV−visible spectrophotometer. (ii) The powder X-ray diffraction patterns were recorded using the Rigaku 2028 Cu Kα X-ray diffractometer and Bruker D8 Advance diffractometer. (iii) The PL spectrum was obtained using a Perkin-Elmer luminescence spectrophotometer (model LS50B). The excitation wavelength was 380 nm. (iv) Transmission and diffuse reflection spectroscopy measurements were carried out on a Cary (varian 1E) spectrophotometer.

3. Preparation of ZnSe Nanoparticles. $Zn(Ac)_2$ (450 mg) and 240 mg of selenourea were dissolved in 70 mL of doubly distilled water and were sonicated for 1 h under an atmosphere of argon, at room temperature. A round-bottom Pyrex glass vessel (total volume 70 mL) was used for the ultrasound irradiation. The temperature of the mixture rose gradually to 80 °C during ultrasonic irradiation. After 1 h of sonication, the solution was centrifuged, and precipitate was washed with water and then with absolute ethanol. A yellow powder was obtained.

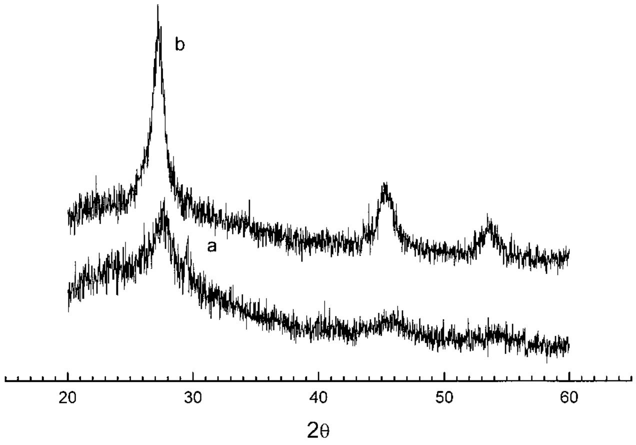

Figure 1. X-ray diffraction pattern of (a) as-prepared ZnSe nanoparticles and (b) ZnSe nanoparticles heated at 500 °C.

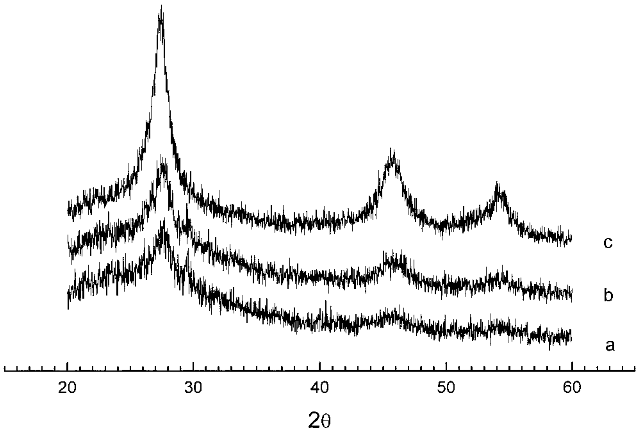

Figure 2. X-ray diffraction patterns of the as-prepared ZnSe after sonication of (a) 1, (b) 2, and (c) 3 h.

3. Results and Discussion

XRD, EDAX, and TEM studies. The XRD pattern of the as-prepared ZnSe showed the presence of broad peaks (Figure 1a), the diffraction peaks corresponding to the (111), (220), and (311) planes of sphalerite-type ZnSe. The broad peaks indicate that the crystal size is small. The size of the ZnSe nanoparticles estimated from Debye−Scherer formula[39] is 3 nm. After the powder was annealed at 500 °C under a flow of Ar for 5 h, sharper peaks appeared in the XRD spectrum (Figure 1b); the calculated size of the annealed ZnSe is bigger, that is, about 6 nm. When the powder was heated for 48 h at the same temperature, the powder size remained unchanged, as deduced from XRD measurements. We found that sonication time also influenced the size. Figure 2 shows the results of different sonication time. After 1, 2, and 3 h of sonication, ZnSe nanoparticles

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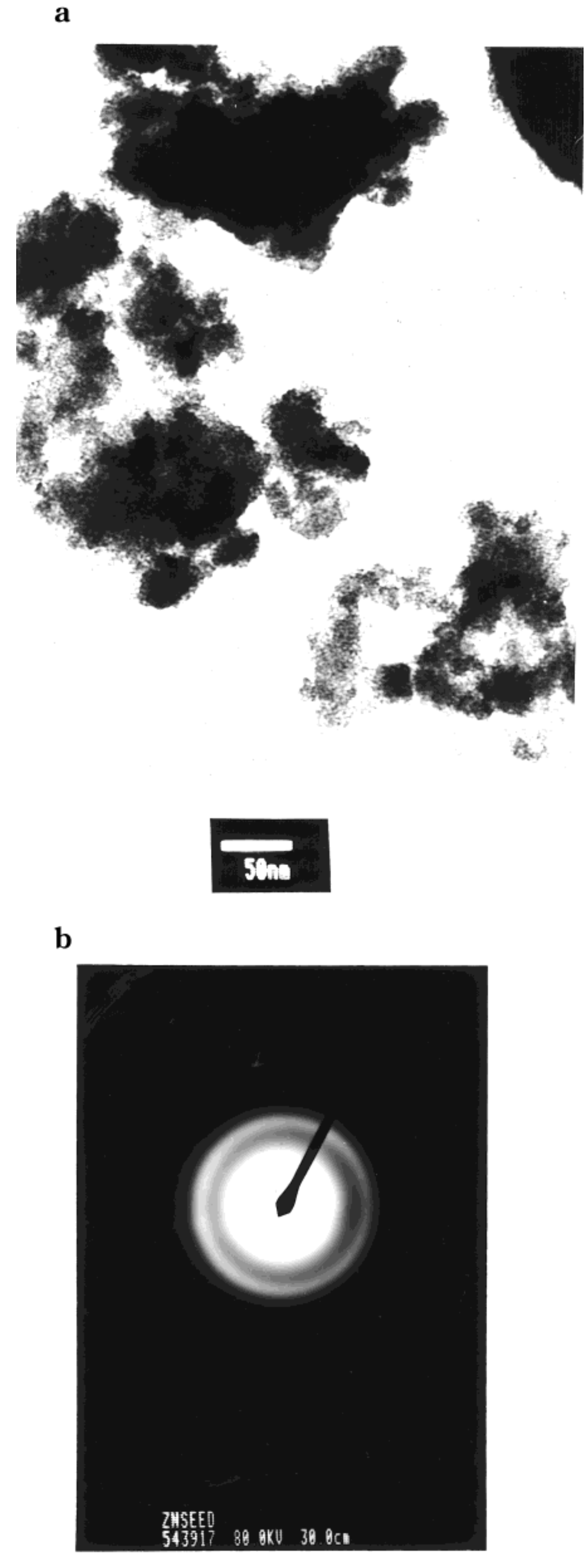

Figure 3. (a) Transmission electron micrograph of the as-prepared ZnSe nanoparticles and (b) electron diffraction pattern of the as-prepared ZnSe nanoparticles.

were about 3, 4, and 5 nm, respectively. We also found that after sonication of the solution for more than 3 h the size remained at 5 nm. The increase of the particle size with sonication time can be explained in terms of the effect of acoustic cavitation on ZnSe. The implosive collapse of a cavity on an extend solid surface in a liquid has been recognized to be different from the symmetrical implosion of cavities observed in homogeneous, pure liquids.[40] In the former case, asymmetric implosion results in the formation of high-speed microjets of liquids as well as shock waves that drive the solid particles to high velocities, which leads to interparticle collisions. The collisions of ZnSe particles at high velocities result in increased local heating and condensation to form larger particles.[41] The increase in size of ZnSe nanoparticles can also involve ZnSe crystal growth. When the ZnSe nanoparticles formed, smaller particles had the large number of dangling bonds, defect sites, or traps.[42] During the reaction time, the surface states change. Dangling bonds, defect sites, or traps will decrease gradually, and particles will grow. After some time, the surface states becomes stable; therefore, the size of ZnSe nanoparticles does not increase.

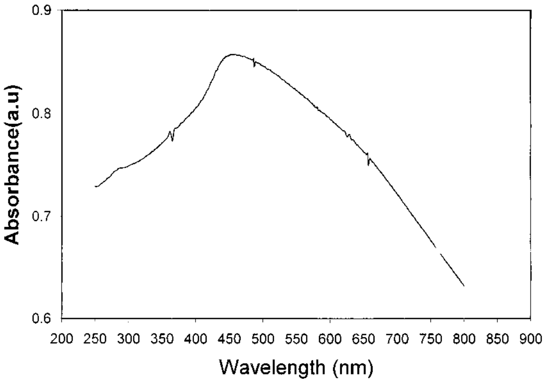

Figure 4. Absorption spectrum of an ethanol solution containing ZnSe nanoparticles.

The EDX pattern for the ZnSe showed the presence of Zn and Se peaks. The average atomic ratio of Zn:Se was 3:2, which showed that the samples were rich in zinc. Similar results have been reported previously for ZnSe.[29,37]

The TEM observations for the as-prepared ZnSe nanoparticles are shown in Figure 3a. It is apparent that ZnSe nanoparticles are spherical and that the particles are held together by a porous, irregular network. A more carefully analysis reveals that these plates have been mostly formed by the aggregation. The average size of these nanoparticles is in the range of 1−5 nm, which is in good agreement with the XRD result. Figure 3b is an electron diffraction (ED) picture. ED measurements show that the particles are partly amorphous.

Optical Properties. UV−visible absorption spectra (Figure 4) of ZnSe nanoparticles dispersed in ethanol solution showed a strong, broad absorption peak center at about 455 nm. The band can be attributed to a surface state of ZnSe nanoparticles because the absorption lies below the absorption edge of the particles and the absorption energy is lower than the band gap of the particle. The large fraction of surface atoms leads to the large number of dangling bonds and stoichiometric or external defects originating from the surface transition.[42,43,44]

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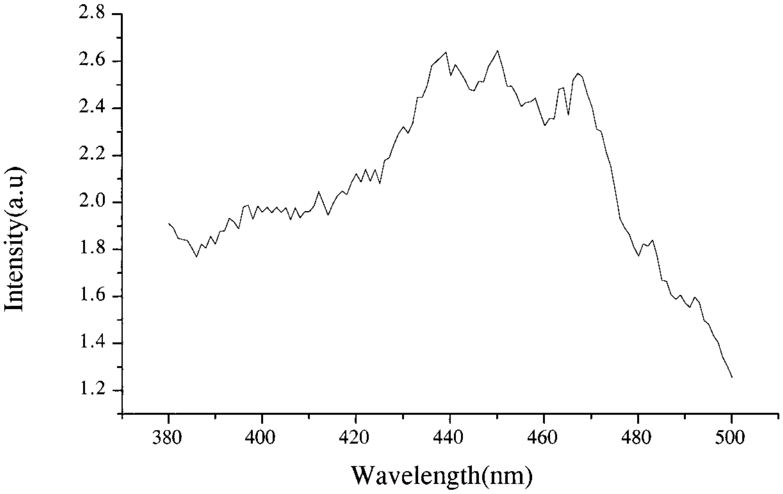

Figure 5. PL spectrum of an ethanol solution containing ZnSe nanoparticles. The excitation wavelength is 380 nm.

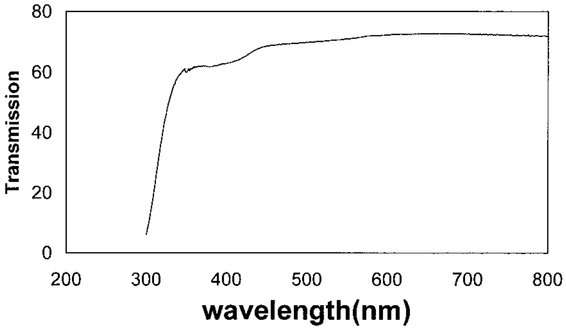

Figure 6. Transmission spectroscopy of a glass coated with ZnSe nanoparticles.

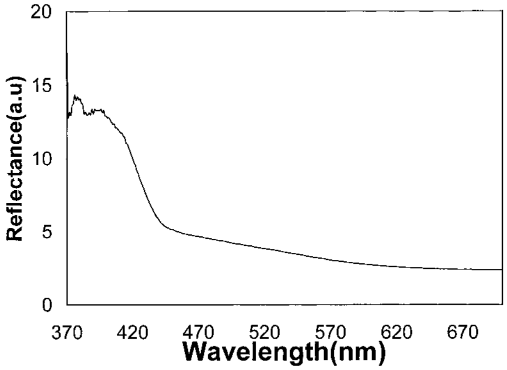

Figure 7. Diffuse reflection spectroscopy of a glass coated with ZnSe nanoparticles.

Figure 5 shows the PL spectra of an ethanol solution containing ZnSe nanoparticles. The PL spectrum of the ZnSe showed a broad emission band peak center at 455 ± 5 nm, using a 380 nm excitation wavelength. Due to the broad nature of the peak, it is difficult to state clearly that a blueshift is detected. It is still worth notice that for bulk ZnSe that peak is observed at 465 nm.[45] The broader peak may be indicative of size quantization.[46,47]

We carried out the transmission and diffuse reflection spectra measurement of ZnSe powder in order to resolve the excitonic or interband (valence–conduction band) transitions of ZnSe, which allow us to calculate the band gap. Figures 6 and 7 are the optical transmission and reflection spectroscopy of the ZnSe powder, respectively. From transmission and DRS spectra, we calculated the band gap of ZnSe to be 2.80 ev. The value of the band gap energy is larger than that reported for bulk ZnSe (2.58 ev),[48] but it is similar to results reported for ZnSe nanoparticles.[37,49,50]

The DSC spectrum presented in Figure 8 reveals a distinct exothermic peak at 430 °C. At first glance, we tried to attribute this peak to the sphalerite-type hexagonal phase transition of ZnSe. However, upon cooling of the sample, it became clear that the transition was not reversible. When the sample was reheated, a flat DSC curve was recorded. We attributed this peak to the amorphous-to-crystalline transition. That would mean that the as-prepared material is a mixture of amorphous and crystalline (sphalerite-type) ZnSe. This is not surprising, because sonochemistry in many cases leads to the formation of amorphous materials.[14,19,20] To confirm this interpretation, we have measured the temperature dependence of the XRD spectrum (Figure 9). The general picture is that of sphalerite-type ZnSe. The intensity and shape of the diffraction peaks were almost unchanged in the 25–300 °C range. When the temperature is increased from 300 to 650 °C, we can observe that the intensity of peaks increase and shifts to slightly low angles. This indicates that amorphous ZnSe nanoparticles were originally present. This is generally consistent with the DSC results. Some references reported also showed similar results.[29,30,37] The amount of the amorphous ZnSe in the as-prepared material is estimated from the XRD peak areas as ca. 15%. We also obtained the result from ED measurements.

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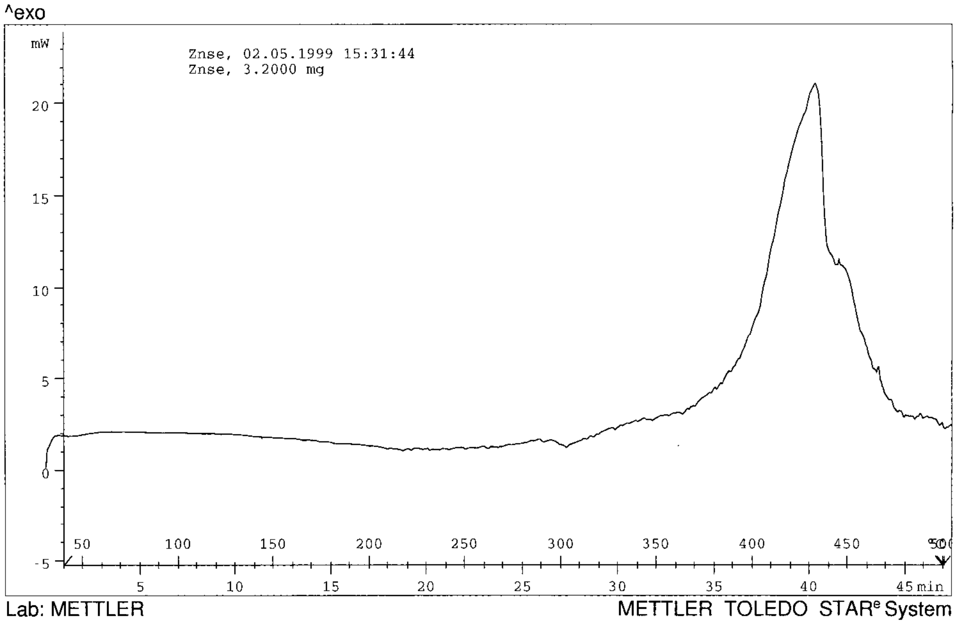

Figure 8. DSC spectrum of the ZnSe nanoparticles. The heating rate is 10 °C/min.

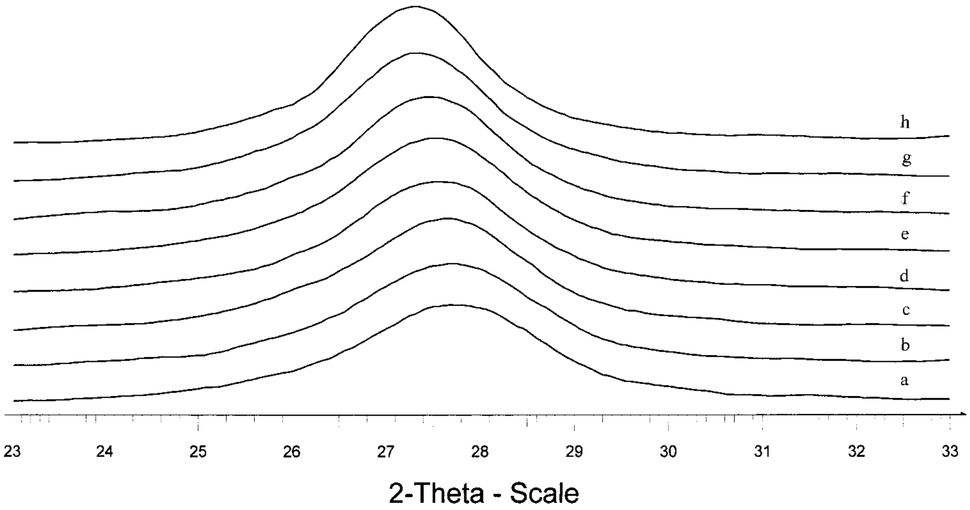

Figure 9. XRD patterns as a function of temperature: (a) 300, (b) 350, (c) 400, (d) 450, (e) 500, (f) 550, (g) 600, and (h) 650 °C.

Ultrasonic waves that are intense enough to produce cavitation can drive chemical reactions such as oxidation, reduction, dissolution, and decomposition.[13,51] Other reactions, such as promotion of polymerization, have also been reportedly induced by ultrasound. It has been known that three different regions[51] are formed during the aqueous sonochemical process: (a) the inner environment (gas phase) of the collapsing bubble, where elevated temperatures (several thousands of degrees) and pressures (hundreds of atmospheres) are produced, causing water to vaporize and further to pyrolyze into H and OH radicals; (b) the interfacial region where the temperature is lower than in the gas-phase region but still high enough to induce a sonochemical reaction; and (c) the bulk solution, which is at ambient temperatures. Among the above-mentioned three regions, it appears that the current sonochemical reaction occurs within the interfacial region, yielding nanoparticles, because of the very high quenching rate experienced by the products. This is because zinc acetate is better described as a somewate ionic compound; it is certainly involatile under normal conditions, but it might well dissociate or produce radicals under the extreme conditions of sonification.

The mechanism of the formation of ZnSe nanoparticles takes into consideration the radical species generated from water molecules by the absorption of ultrasound energy. The likely reaction steps and explanation for the sonochemical reduction process can be summarized as follows:

$$\mathrm{H_2O}\ )))))\ \mathrm{H^\bullet + OH^\bullet} \qquad (1)$$

$$\mathrm{2H^\bullet + RSe \rightarrow H_2Se + R^\bullet} \qquad (\mathrm{R{=}NH_2CNH_2}) \quad (2)$$

$$\mathrm{H_2Se + Zn(Ac)_2 \rightarrow ZnSe + 2HAc} \qquad (3)$$

Equation 1 represents the formation of primary radicals by the ultrasound-initiated dissociation of water; then, H_2Se formed by eq 2 combines with Zn-$(Ac)_2$ via eq 3 to yield ZnSe nanoparticles. Another

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possibility is explained as follows: The cleavage of water could be linked with addition across the C═Se bond to give $(NH_2)_2C(OH)-SeH$. Repeating this process would then result in formation of $(NH_2)_2C(OH)_2$ (which would immediately lose water to give urea, $(NH_2)_2C{=}O$) and H_2Se, and then H_2Se would react with $Zn(Ac)_2$ via eq 3 to yield ZnSe nanoparticles.

4. Conclusion

ZnSe nanoparticles have been prepared by the sonochemical method. The advantages of this process are that it is a simple and efficient method to produce nanoparticles that are very small in size (around 3 nm). These nanoparticles could find use in solar cells, in modern electronics and electrooptical devices. Replacing the $Zn(Ac)_2$ by $Cu(Ac)_2$ or by $Pb(Ac)_2$ yielded nanoparticles of CuSe and PbSe, respectively.

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