

# Preparation of Nanoscale Semiconductors through the Rapid Expansion of Supercritical Solution (RESS) into Liquid Solution

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The preparation of nanoscale lead sulfide (PbS) particles using a supercritical fluid processing technique is reported. The method is based on two simultaneous modifications to the conventional RESS (rapid expansion of supercritical solution) process. The first is to expand the supercritical solution into a liquid solution instead of a gas, and the second is to use a reacting system, in which one reactant is dissolved in the supercritical solution and one in the liquid receiving solution. Supercritical ammonia, methanol, and acetone solutions are used for rapid expansion, and the PbS nanoparticles obtained with the different solvents are rather similar. RESS experiments are also carried out under different experimental conditions, but the changes in processing parameters apparently have only marginal effects on the produced PbS nanoparticles. Mechanistic considerations on the RESS into solution method and issues concerning the use of the semiconductor nanoparticles in nanocomposite materials are discussed.

## Introduction

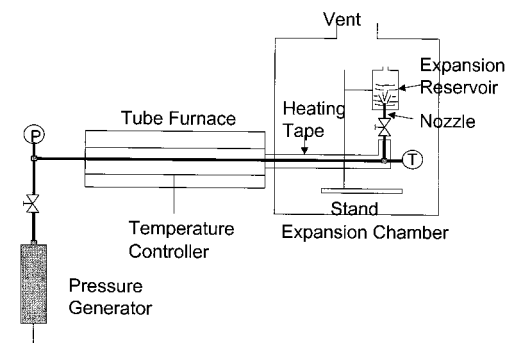
Nanoscale materials have attracted much recent attention for their unique chemical and physical characteristics.<sup>1,2</sup> For semiconductor nanoparticles, their electronic and optoelectronic properties are dramatically different from those of the corresponding bulk solids.<sup>2</sup> Potential applications of nanoscale semiconductors, including uses as photosensitizers in photovoltaic devices and photocatalytic systems, have also been widely discussed.<sup>3,4</sup> These applications require the development of synthetic methodologies that are versatile, efficient, and economic. Several experimental techniques have been reported in the literature for the preparation and immobilization of nanoscale semiconductor particles.<sup>1–3,5–11</sup> Among the most convenient is the mixing of solutions under ambient conditions; a classic example is the mixing of a cadmium cation solution with a sulfide anion solution at room temperature to produce cadmium sulfide particles. However, this simple mixing method typically requires other reagents or subsequent treatment such as selective precipitation to yield nanoparticles with desirable properties.<sup>12</sup> Other methods for semiconductor nanoparticle preparation include those based on the use of reverse micelles<sup>13–15</sup> and sonochemical decomposition of precursor mixtures.<sup>8,16</sup> We have recently reported the preparation of nanoscale semiconductor and metal particles via the application of supercritical fluid processing technology.<sup>17–20</sup> Our method is based on two simultaneous modifications to the conventional RESS (rapid expansion of supercritical solution) process.<sup>21–26</sup> First, we expand the supercritical solution into a liquid solution instead of a gas. Second, we use a reacting system, in which one reactant is dissolved in the supercritical solution and one in the liquid receiving solution. The nanoparticles obtained via our method of RESS into solution are in the size domain of a few nanometers, with relatively narrow size distributions.<sup>21–26</sup> Here we report the preparation of nanoscale lead sulfide (PbS) particles via the RESS into solution method. In the nanoparticle preparation, the experimental conditions were systematically varied, so

that effects of processing parameters on properties of the nanoparticles thus produced could be evaluated. The characterization of the nanoparticles included applications of UV–vis absorption spectroscopy, X-ray powder diffraction, and transmission electron microscopy (TEM) techniques. Mechanistic considerations on the RESS into solution method and issues concerning the use of the semiconductor nanoparticles in nanocomposite materials are discussed.

## Experimental Section

**Materials.** Lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) was purchased from Fisher Scientific, and sodium sulfide ( $\text{Na}_2\text{S}$ ) was obtained from Aldrich. Anhydrous ammonia (purity > 99.9999%) was purchased from Air Products and was dried and filtered before use. Methanol and acetone were obtained from Mallinckrodt and were filtered before use. Absolute ethanol was purchased from Fisher Scientific and was distilled over molecular sieves and filtered before use. Water was deionized and purified by being passed through a Labconco WaterPros water purification system. Poly(*N*-vinyl-2-pyrrolidone) (PVP) of average molecular weight  $M_n \sim 360\,000$  was obtained from Sigma and used without further purification.

**Measurements.** The apparatus for producing nanoparticles via the RESS into solution method is illustrated in Figure 1. It consists of a syringe pump for the pressure generation and maintenance during RESS and a gauge for monitoring the system pressure. The heating unit consists of a cylindrical solid copper block of high heat capacity coiled around by a long section of stainless steel tubing, and the copper block–tubing coil assembly is hosted tightly in a stainless steel tube to ensure close contacts between the tubing coil and the copper block for efficient heat transfer. The whole unit is located in a tube furnace. Before each RESS experiment, the heating unit is equilibrated at the preset temperature. For the use of a solvent with high critical temperature, the syringe pump can be preheated to ensure that the supercritical solution is thermally equilibrated at the preset temperature before reaching



**Figure 1.** Experimental apparatus for the preparation of nanoparticles via the RESS into solution method.

the nozzle for rapid expansion. The expansion nozzle is a fused silica capillary hosted in a stainless steel tubing, and the nozzle is inserted into the RESS chamber containing an ambient solution.

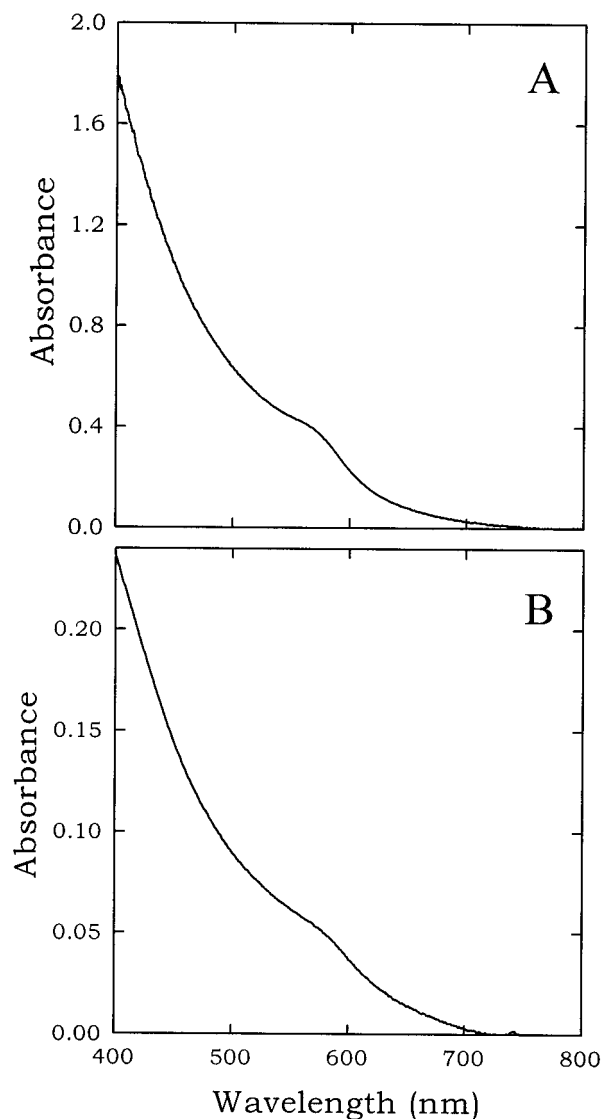
UV-vis absorption spectra were obtained on a computer-controlled Shimadzu UV-2101PC spectrophotometer. UV-vis diffuse reflectance measurements were carried out using a Shimadzu UV-3100 spectrophotometer equipped with the ISR-3100 diffuse reflectance attachment. Steady-state luminescence measurements were performed on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450-W xenon source and an R928 photomultiplier tube as the detector. X-ray powder diffraction patterns were determined on a Scintag XDS-2000 powder diffraction system. TEM images were obtained using a Hitachi 600AB 100 kV transmission electron microscope.

## Results and Discussion

Nanoscale PbS particles were prepared via the RESS into solution method under different experimental conditions and were characterized both in suspension and in the solid state.

**Rapid Expansion of a Supercritical Ammonia/Pb(NO<sub>3</sub>)<sub>2</sub> Solution.** In a typical experiment, a homogeneous solution of Pb(NO<sub>3</sub>)<sub>2</sub> in liquid ammonia (0.5 mg/mL) was prepared in the syringe pump as follows: a solution of Pb(NO<sub>3</sub>)<sub>2</sub> in methanol was added to the pump, followed by the evaporation of the solvent methanol and then the addition of liquid ammonia. The solution was then heated in the heating unit to the preset temperature before reaching the expansion nozzle. Finally, the supercritical ammonia/Pb(NO<sub>3</sub>)<sub>2</sub> solution at 160 °C and 3500 psia was rapidly expanded through a fused silica capillary nozzle of 50 μm inner diameter into the expansion chamber, which contained a room-temperature solution of Na<sub>2</sub>S in ethanol, to produce PbS nanoparticles. The room-temperature solution in the expansion chamber also contained PVP polymer (6 mg/mL) for stabilizing the suspension of the produced PbS nanoparticles.

The UV-vis absorption spectrum of the PbS nanoparticles suspended in ethanol is shown in Figure 2A. Despite being a suspension, the effect of scattering was negligible in the absorption measurement because the particles were nanoscopic. Thus, there was no need for the use of UV-vis diffuse reflectance attachment. The absorption onset of the suspended PbS nanoparticles is at ~700 nm, with a clear shoulder at ~550 nm (Figure 2A). As reported in the literature,<sup>2,27</sup> PbS is a narrow band gap semiconductor, with the onset of electronic

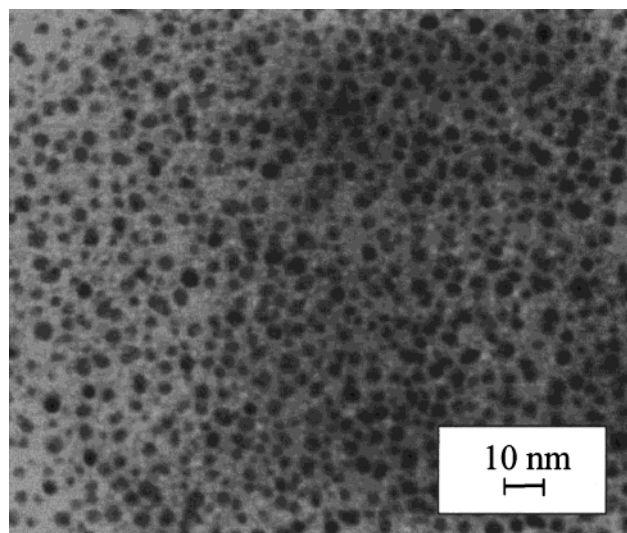


**Figure 2.** UV-vis absorption spectra of the PbS nanoparticles obtained via the rapid expansion of (A) a supercritical ammonia/Pb(NO<sub>3</sub>)<sub>2</sub> solution and (B) a supercritical acetone/Pb(NO<sub>3</sub>)<sub>2</sub> solution into a room-temperature solution of Na<sub>2</sub>S in ethanol.

transition being in the infrared for the bulk material. The absorption spectrum undergoes a dramatic blue shift as the PbS particle size decreases, exhibiting an extreme quantum confinement effect.<sup>2,27</sup> According to a rough empirical correlation between the particle size and the absorption spectral position,<sup>27</sup> the absorption result in Figure 2A corresponds to PbS particles of sizes in the 2.5–4 nm range.

The average size and size distribution of the PbS nanoparticles were determined via TEM analysis. For the TEM measurement, the nanoparticle suspension in ethanol was first diluted and then deposited via evaporating the solvent ethanol on a colloidal film supported by a copper grid. Shown in Figure 3 is a typical TEM image of the PbS nanoparticles, from which an average particle size of 4 nm and a size distribution standard deviation of 0.7 nm were obtained.

In principle, the average size of the PbS nanoparticles can also be estimated in terms of X-ray powder diffraction results. In the experiment, a solid-state sample of the PbS nanoparticles was obtained from the ethanol suspension by evaporating the solvent, repeated washing with clean water, and then drying in a vacuum oven.



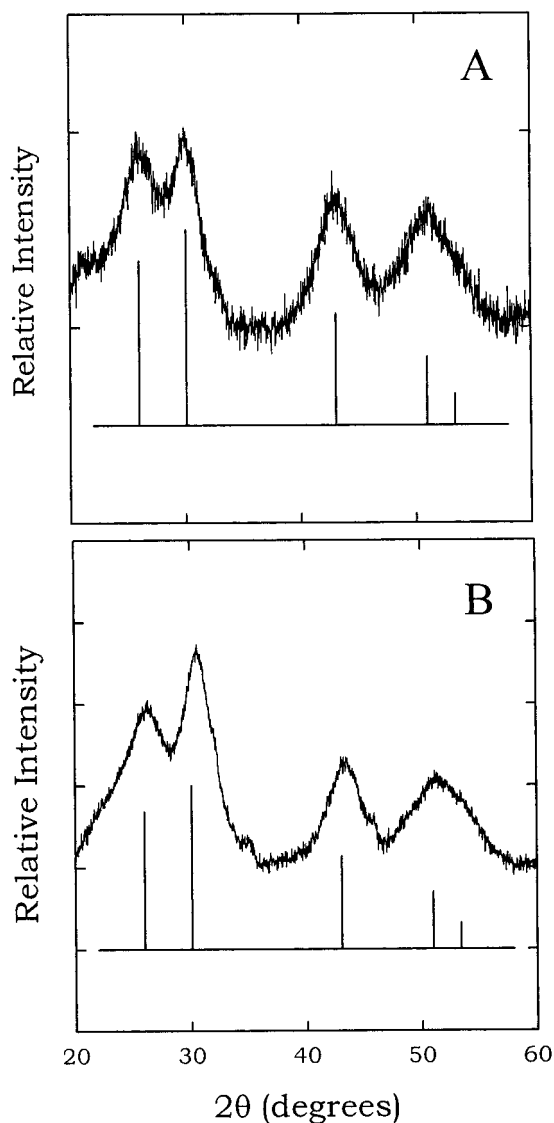
**Figure 3.** TEM image of the PbS nanoparticles obtained via the rapid expansion of a supercritical ammonia/Pb(NO<sub>3</sub>)<sub>2</sub> solution into a room-temperature solution of Na<sub>2</sub>S in ethanol.

A typical X-ray powder diffraction pattern of the PbS nanoparticles is shown in Figure 4A, which matches well with the PbS reference in the JCPDS (Joint Committee on Powder Diffraction Standards) database. The broadness in observed diffraction peaks is characteristic of the PbS particles being nanoscopic, and the diffraction peak broadening may be related to the average particle size in terms of the Debye–Scherer equation<sup>28</sup>

$$D = K\lambda/(\beta \cos \theta) \quad (1)$$

where  $D$  is the average particle diameter in angstroms,  $\beta$  is the corrected band broadening (fwhm),  $K$  is a constant related to the crystallite shape and the way in which  $D$  and  $\beta$  are defined,  $\lambda$  is the X-ray wavelength, and  $\theta$  is the diffraction angle. For the diffraction pattern of the PbS nanoparticles shown in Figure 4A, the average particle size thus calculated is 2.7 nm, which is significantly smaller than the value obtained from the TEM analysis. Such disagreement between the results from X-ray and TEM is common in the characterization of nanoscale semiconductors. A major contribution to the disagreement is probably from the calculation in terms of eq 1, which operates under the assumption that the peak broadening in X-ray powder diffraction pattern is due entirely to the reduction in particle size. In reality, however, these small PbS nanoparticles are probably partially amorphous, which also contributes to the diffraction peak broadening and, consequently, to the error in using eq 1 to estimate the average particle size. Thus, the TEM result likely reflects more accurately the physical parameters of the PbS nanoparticles.

We reported previously that the cadmium sulfide (CdS) nanoparticles prepared via the rapid expansion of a supercritical ammonia/Cd(NO<sub>3</sub>)<sub>2</sub> solution have interesting luminescence properties, with the absence of the long-wavelength luminescence band commonly observed for CdS nanoparticles.<sup>17,20</sup> Because the red luminescence band is typically related to the trapping of excitation energy by surface defects such as dangling bonds and vacancies,<sup>2</sup> luminescence results of the CdS nanoparticles obtained via the RESS into solution method were discussed in terms of surface passivation



**Figure 4.** X-ray powder diffraction patterns of the PbS nanoparticles obtained via the rapid expansion of (A) a supercritical ammonia/Pb(NO<sub>3</sub>)<sub>2</sub> solution and (B) a supercritical methanol/Pb(NO<sub>3</sub>)<sub>2</sub> solution into a room-temperature solution of Na<sub>2</sub>S in ethanol. The pattern for bulk PbS in the JCPDS database is also shown for comparison.

effects associated with the rapid expansion of supercritical ammonia solution.<sup>17,20</sup> For PbS nanoparticles, the consensus in the literature seems to be that they are nonluminescent. However, there was a report that showed luminescence spectra of PbS nanoparticles, where the particles were prepared by a solution-based method.<sup>29</sup> Thus, we made a significant effort to detect luminescence from our PbS nanoparticles produced via the RESS into solution method. The measurements were carried out on our photon-counting emission spectrometer that is capable of detecting extremely weak luminescence of yield as low as 10<sup>-5</sup>. Even with the use of supercritical ammonia, no luminescence was observed for the PbS nanoparticles suspended in room-temperature ethanol. However, in that paper,<sup>29</sup> it was discussed that the luminescence of colloidal PbS responds in an extremely sensitive manner to chemical changes on the surface of the particles. Perhaps PbS nanoparticles require a kind of surface passivation different from that of CdS nanoparticles with respect to their luminescence properties.



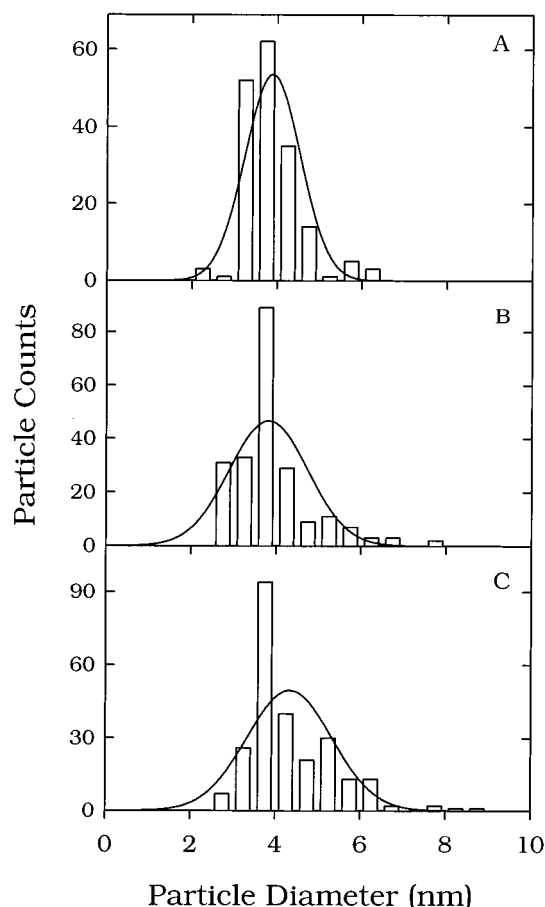
**Effects of RESS Parameters.** PbS is one of the semiconductors that exhibits an extreme quantum confinement effect, with the absorption spectral properties highly sensitive to the physical parameters of the nanoparticles. Thus, for the RESS into solution method, effects of RESS parameters on the produced nanoparticles may be evaluated via systematically investigating the properties of the PbS nanoparticles obtained under different experimental conditions.

**(a) Temperature of the Supercritical Ammonia/ $\text{Pb}(\text{NO}_3)_2$  Solution.** PbS nanoparticles were prepared via the rapid expansion of a supercritical ammonia/ $\text{Pb}(\text{NO}_3)_2$  solution at different temperatures. In the experiments, all parameters including  $\text{Pb}(\text{NO}_3)_2$  concentration, expansion nozzle size, and concentrations of  $\text{Na}_2\text{S}$  and PVP polymer in the room-temperature ethanol solution were kept constant, except for the temperature of the ammonia/ $\text{Pb}(\text{NO}_3)_2$  solution for rapid expansion. The PbS nanoparticles obtained via the rapid expansions at 160 and 130 °C were characterized and compared. The absorption spectra of the two PbS nanoparticle samples are quite similar, indicating that the absorption properties of the nanoparticles are insensitive to the change in RESS temperature. Because the band gap in PbS nanoparticles is strongly dependent on the average particle size, the similarity in observed absorption properties reflects the fact that the PbS nanoparticles obtained by RESS at the two different temperatures have similar sizes. This is confirmed by the results from X-ray powder diffraction measurements of the PbS nanoparticles, where the diffraction patterns of the two nanoparticle samples are also similar.

**(b) Nozzle Size.** With the other experimental parameters kept constant, rapid expansions of a supercritical ammonia/ $\text{Pb}(\text{NO}_3)_2$  solution were carried out using nozzles of different sizes. The nozzles were fused silica capillaries with inner diameters of 19, 50, and 77  $\mu\text{m}$ . Because the operating pressure was maintained at close to the designated value (3500 psia) during the RESS process, a smaller nozzle size resulted in a slower expansion. However, despite the significant difference in the rate of supercritical solution expansion, similar PbS nanoparticles were obtained.

UV-vis absorption spectra of the three PbS nanoparticle samples obtained by RESS with different expansion nozzle sizes are similar, indicative of their similar average particle sizes. This is confirmed by results from the TEM analysis of the three samples, and the corresponding histograms are compared in Figure 5. Apparently, the average sizes of the PbS nanoparticles produced via the use of three different expansion nozzle sizes are only marginally different, with all of them around 4 nm (Figure 5 and Table 1). Thus, it is probably safe to conclude that the expansion nozzle size affects only marginally the properties of the PbS nanoparticles thus produced.<sup>30</sup>

**RESS with Other Solvents.**<sup>31</sup> PdS nanoparticles were also prepared via the rapid expansion of other supercritical solutions. For example, methanol was used to replace ammonia for the preparation of a homogeneous methanol solution of  $\text{Pb}(\text{NO}_3)_2$  (0.7 mg/mL) in the syringe pump. After the solution was heated to the preset temperature in the heating unit of the experimental apparatus (Figure 1), the supercritical methanol/ $\text{Pb}(\text{NO}_3)_2$  solution at 250 °C and 3500 psia was rapidly expanded through a fused silica capillary nozzle into the expansion chamber, which contained a room-tempera-



**Figure 5.** Histograms from TEM images of the PbS nanoparticles prepared with ammonia expansions using nozzles of (A) 19, (B) 50, and (C) 77  $\mu\text{m}$  inner diameters. The average particle size and size distribution values are shown in Table 1.

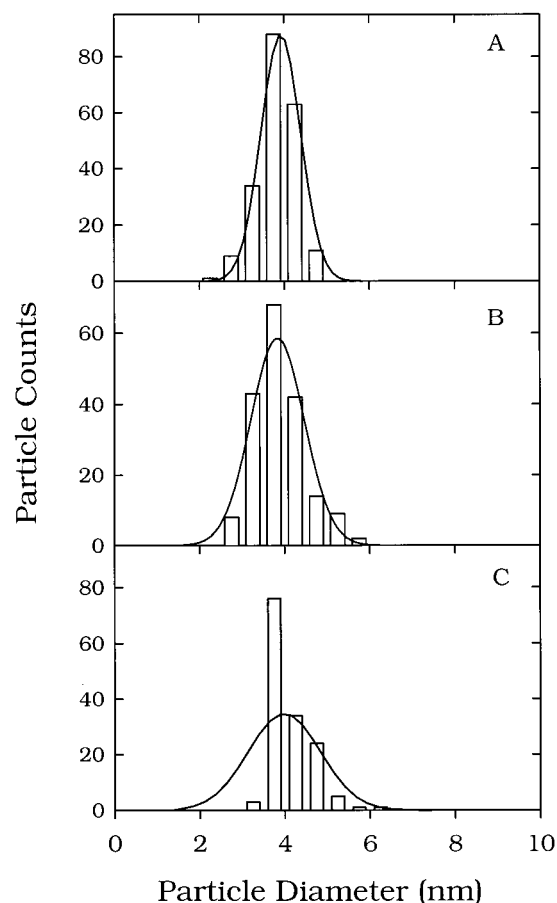
**Table 1. Comparison of PbS Nanoparticles Produced under Different Conditions<sup>a</sup>**

solvent	19 $\mu\text{m}$ nozzle		50 $\mu\text{m}$ nozzle		77 $\mu\text{m}$ nozzle	
	D, nm	$\sigma$ , nm	D, nm	$\sigma$ , nm	D, nm	$\sigma$ , nm
ammonia	3.9	0.65	3.9	0.7	4.3	0.8
methanol	4.1	0.5	3.9	0.6	4.2	0.8
acetone	4.5	0.7	4.1	0.8	4.6	1

<sup>a</sup> The average particle size in diameter ( $D$ , nm) and the size distribution standard deviation ( $\sigma$ , nm) were determined via TEM analyses.

ture solution of  $\text{Na}_2\text{S}$  and PVP polymer in ethanol. The PbS nanoparticles thus obtained were characterized, and the results were analyzed in reference to those of the PbS nanoparticles produced via the ammonia expansion. The absorption spectrum of the PbS nanoparticles obtained with the methanol expansion is similar to that of the particles obtained with the ammonia expansion and so is the X-ray powder diffraction pattern (Figure 4B). A TEM analysis of the PbS nanoparticles obtained with the methanol expansion yielded an average particle size of 3.9 nm and a size distribution standard deviation of 0.6 nm (Figure 6). Again, the results are similar to those of the PbS nanoparticles obtained with the ammonia expansion.

For the rapid expansion of a supercritical methanol/ $\text{Pb}(\text{NO}_3)_2$  solution, effects of the nozzle size on nanoparticle properties were also examined by keeping the other experimental parameters constant. The PbS nanoparticles thus produced with different nozzles all have similar UV-vis absorption properties. As compared in

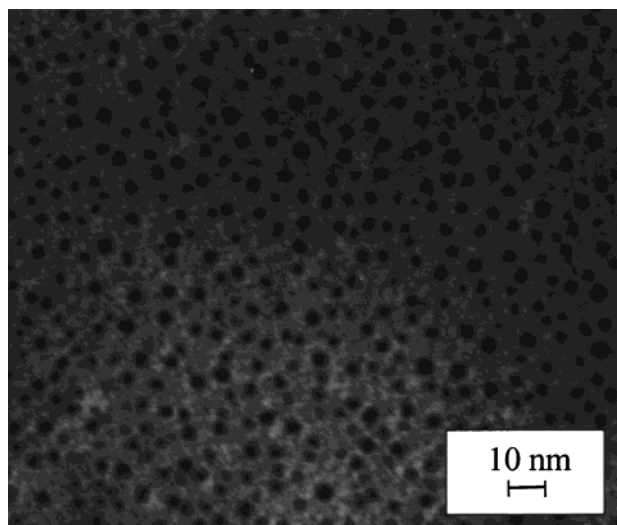


**Figure 6.** Histograms from TEM images of the PbS nanoparticles prepared with methanol expansions using nozzles of (A) 19, (B) 50, and (C) 77  $\mu\text{m}$  inner diameters. The average particle size and size distribution values are shown in Table 1.

Figure 6 and Table 1, the TEM results of the samples obtained with different nozzles in the methanol expansion are not only similar among themselves but also similar to those of the PbS nanoparticles prepared with the ammonia expansion.

In addition to methanol, acetone was used with the RESS into solution method as well. The rapid expansion of a supercritical acetone/ $\text{Pb}(\text{NO}_3)_2$  solution at 250  $^\circ\text{C}$  and 3500 psia into a room-temperature ethanol solution of  $\text{Na}_2\text{S}$  also resulted in the formation of PbS nanoparticles. According to the UV-vis absorption (Figure 2B) and TEM (Figure 7) results, the PbS nanoparticles thus produced are again similar to those obtained with the ammonia and methanol expansions discussed above. Finally, the acetone expansions with different nozzle sizes also resulted in similar PbS nanoparticles (Table 1).

**Mechanistic and Other Considerations.** The RESS into solution method for the preparation of nanoparticles might be understood in terms of the same mechanistic framework as that for the conventional RESS production of micron-sized (submicron-sized in some cases) particles.<sup>21–26</sup> A possible scenario is that the formation of PbS nanoparticles is through the reaction of  $\text{S}^{2-}$  species with the  $\text{Pb}^{2+}$  species in nanoscopic “solute droplets” that are produced in the RESS process. With conventional RESS, the solute  $\text{Pb}(\text{NO}_3)_2$  would rapidly precipitate out of the supercritical solution to form initially species that may be considered as “solute droplets”, and then these nanoscopic species form micron-sized (submicron-sized in some cases) particles

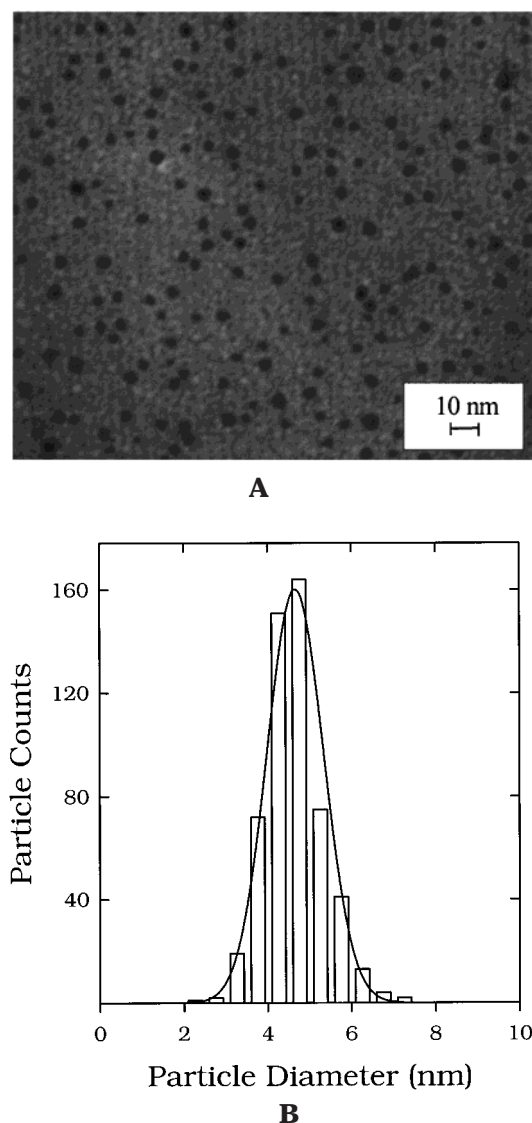


**Figure 7.** TEM image of the PbS nanoparticles obtained via the rapid expansion of a supercritical acetone/ $\text{Pb}(\text{NO}_3)_2$  solution into a room-temperature solution of  $\text{Na}_2\text{S}$  in ethanol.

via agglomeration.<sup>32</sup> However, the receiving liquid in the RESS into solution process may temporarily stabilize the initially formed nanoscopic “solute droplets” to allow their capture by the reactant species ( $\text{S}^{2-}$ ) in the same receiving solution. Here, the role of PVP polymer is suspension stabilization after the nanoparticle formation. In fact, PbS nanoparticles can also be prepared via the RESS into solution method in the absence of PVP polymer, though it is still needed thereafter for the suspension stabilization over an extended period of time. These PbS nanoparticles prepared without PVP polymer are essentially the same as those obtained in the presence of PVP polymer during the rapid expansion. In addition to PVP polymer, other stabilization agents such as aliphatic and aromatic thiols can also be used with the RESS into solution method for nanoscale semiconductors.<sup>33</sup>

The formation of PbS nanoparticles is apparently insensitive to the changes in experimental parameters with the RESS into solution method. The nanoparticle properties, including average particle size, size distribution, and related UV-vis absorption and X-ray diffraction patterns, show only marginal variations with the changes in RESS processing conditions. In addition, the preparation of PbS nanoparticles is also independent of whether the cationic or anionic species is in the supercritical solution. In fact, the rapid expansion of a supercritical methanol/ $\text{Na}_2\text{S}$  solution into a room-temperature solution of  $\text{Pb}(\text{NO}_3)_2$  in ethanol also resulted in the formation of PbS nanoparticles. The UV-vis absorption, X-ray diffraction, and TEM (Figure 8) results show that the PbS nanoparticles thus produced are rather similar to those obtained via the rapid expansion of a supercritical ammonia/ $\text{Pb}(\text{NO}_3)_2$  solution into a  $\text{Na}_2\text{S}$  solution.

The fact that similar PbS nanoparticles are obtained under a variety of operational conditions points to a useful feature of the RESS into solution method, which allows the production of nanoscale semiconductors in a consistent and reproducible fashion. The negative aspect of the insensitivity toward changes in experimental parameters is that it limits the ability to manipulate the nanoparticle properties via varying the RESS processing conditions. However, it should also be recognized that the changes in experimental parameters



**Figure 8.** (A) TEM image of the PbS nanoparticles obtained via the rapid expansion of a supercritical methanol/ $\text{Na}_2\text{S}$  solution into a room-temperature solution of  $\text{Pb}(\text{NO}_3)_2$  in ethanol. (B) Histogram from the TEM image.

investigated here are relatively narrow, so that the results do not necessarily rule out the possibility of producing nanoparticles of different properties via more dramatic changes in RESS processing parameters.

The PbS nanoparticles produced via the RESS into solution method form homogeneous suspensions under the protection of stabilization agents such as PVP polymer. These suspensions allow the preparation of polymer films embedded with nanoscale semiconductors. An example of such composite materials is the poly(vinylcarbazole) thin film homogeneously dispersed with PbS nanoparticles to be used as an efficient photoconductor.<sup>2,33</sup> Here, poly(vinylcarbazole) as the hosting polymer for the composite film can also be used as a stabilization agent in the nanoparticle suspension to eliminate the need for PVP polymer, which otherwise becomes an impurity in the nanocomposite film.<sup>33</sup>

In summary, nanoscale PbS particles were prepared via the RESS into solution method. Supercritical ammonia, methanol, and acetone were used; and the nanoparticles obtained with the different solvents were rather similar. In addition, RESS experiments were carried out under different experimental conditions, but

the changes in experimental parameters apparently had only marginal effects on the produced PbS nanoparticles. Thus, it is concluded that nanoscale semiconductors such as PbS can be obtained via the RESS into solution method in a consistent and reproducible fashion.

## Acknowledgment

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