



Research article

A study of PbS nanoparticle synthesis via sulfur powder

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Abstract: PbS nanoparticles (NPs) were synthesized by the hot-injection solution-phase method using sulfur powder as precursor. Pb-precursor (446 mg PbO) was dissolved with 1.5 ml oleic acid in 15 ml 1-octadecene (ODE) solvent inside a four-neck flask under N₂ atmosphere and nucleated at 120 °C for half an hour. S-precursor (S powder), dissolved in a mixture of 3 ml ODE and 1 ml Oleylamine, was then injected swiftly by a syringe into the flask with well-dissolved Pb-precursor. The growth time varied from 10 minutes to a few hours and growth temperature was maintained at from 90 to 120 °C after injection, which would result in nanoparticles of different sizes from 5 to 10 nm. The synthesized PbS NPs were characterized by TEM, XRD, and UV-Vis-NIR spectrometer. The morphology as well as absorption spectra were found to be highly sensitive to the synthesis conditions. The XRD spectra showed that the structures were less sensitive to synthesis conditions.

Keywords: synthesis; nanoparticles; hot-injection; characterization; lead sulfide; sulfur powder

1. Introduction

Research on novel nanomaterials and their wide range of applications in almost all branches of sciences and engineering has been in the center of extensive studies for almost two decades now [1]. Successful syntheses of novel nanomaterials and detailed characterizations of physical properties entail promising device and biomedical applications. Lead sulfide (PbS) is a narrow band gap (0.4 eV for bulk material) semiconductor material and its exciton Bohr radius is about 18 nm, making it an ideal material to study quantum confinement at near-infrared (NIR) range [2,3].

Therefore, lead sulfide is a promising material platform to study photovoltaic, thermoelectric, and optoelectronic devices [4,5,6]. There are numerous reports on how to synthesize PbS NPs using different sulfur precursors such as TMS (Bis(trimethylsilyl) sulfide) or H₂S [7–10]. Yet in the literature, synthesis with sulfur powder, a very abundant and inexpensive element, as precursor is scarcely reported [11,12,13]. Achieving successful synthesis of PbS using sulfur as precursor will reduce the material cost significantly. In this paper, we present a recent detailed study on the synthesis conditions (such as growth temperature, growth time, precursor ratio, doping, etc.) of PbS NPs using lead (II) oxide and sulfur powder, as precursors, ODE as solvent, and oleic acid as stabilizer. We observe a strong correlation between morphology of nanoparticles, materials properties, growth temperatures, as well as precursor ratios.

2. Materials and Method

We adopted a nucleation method for PbS NP growth through formation of Pb oleate at the early stage of synthesis [7]. The typical synthesis of PbS NPs is as following: First, the Pb-precursor, 446 mg PbO, and 1.5 ml oleic acid (OA), were well mixed and completely dissolved under continuous stirring in 15 ml organic solvent 1-octadecene (ODE) at a temperature around 120 °C under N₂ atmosphere. The temperature was then adjusted to the desired injection temperature (90 to 150 °C). Second, after mixing for about one hour to ensure complete formation of lead oleate, sulfur powder (32 mg) was dissolved in 3 ml ODE plus 1 ml oleylamine (OAM), was then injected by a syringe at the set temperature and then the temperature was changed from set temperature to the growth temperature (90 to 150 °C). Third, the reaction continued until the desired growth time, then the heating was turned off. Acetone (50 ml) was used to wash and precipitate the synthesized PbS. The precipitated nanoparticles were then dissolved again in Hexane. Other than typical standard synthesis, we also studied the effects of different synthesis conditions. The growth times were varied between 5 minutes to a few hours to observe the different stages of growth of nanoparticles. The growth temperatures were also varied between 90 °C and 150 °C. The precursors ratios of Pb:S were also varied from 2:1 to 4:1 to study the correlation between morphology and precursor ratio. Other precursors such as Manganese (II) acetate was also mixed with PbO to study if Mn²⁺ has any effects on the growth of PbS NPs. Manganese has been studied extensively as transitional metal dopant to introduce magnetic moment in the nanostructures.

Detailed studies of PbS NPs synthesis process via varying injection temperatures, precursor ratios, growth temperatures, growing time, and doping material are very important in understanding the mechanism of the syntheses and thus tailoring the material properties in applications. The as-synthesized nanoparticles were characterized by TEM, XRD and UV-Vis-NIR spectrometer to reveal the effects from growth conditions. The findings based on characterizations by TEM, XRD and UV-Vis-NIR spectrometer will be discussed below. The TEM measurements were done with a JEOL1400 TEM, the XRD measurements were done on PbS NPs powder with a Rigaku Miniflex II, and the absorption spectra were measured in Hexane solution in a quartz cuvette with a Perkin Elmer 750 UV-Vis-NIR spectrometer.

3. Results and Discussion

3.1. TEM

Through TEM images, we come to the conclusion that the morphology of nanoparticles depends heavily on the synthesis conditions. As shown in Figure 1, the sizes and morphology of PbS NPs synthesized under different conditions are imaged with TEM (JEOL 1400). The PbS NPs (Pb:S ~ 2:1) synthesized at 120 °C (Figure 1c) exhibits uniform morphology (more cube-like) after 10 minutes growth; and the NPs (Pb:S ~ 2:1) synthesized at 90 °C (Figure 1a) exhibits almost uniform morphology (more spherical) after 30 minutes growth; whereas the NPs (Pb:S ~ 2:1) synthesized at 90 °C (Figure 1b) exhibits incomplete growth after 10 minutes; and the synthesis with higher Pb:S ratio (Pb:S ~ 4:1) (Figure 1d) exhibits even more incomplete growth after 10 minutes. It can be concluded that for the synthesis with sulfur powder as precursor, to get more uniform morphology, the growth time needs to be at least 30 minutes at 90 °C and 10 minutes at 120 °C, higher growth temperature will require less growth time, and a Pb:S ratio ~2:1 is more beneficial to uniform growth. We also found that when the Pb:S ratio is lower than 2:1 the synthesis was more prone to aggregation so in this paper we focus on lead rich composition only. Generally the growth temperature can be varied from 90 to 150 °C and growth time can be varied from 10 minutes to a few hours. Going above 150 °C or longer than a few hours could cause aggregation.

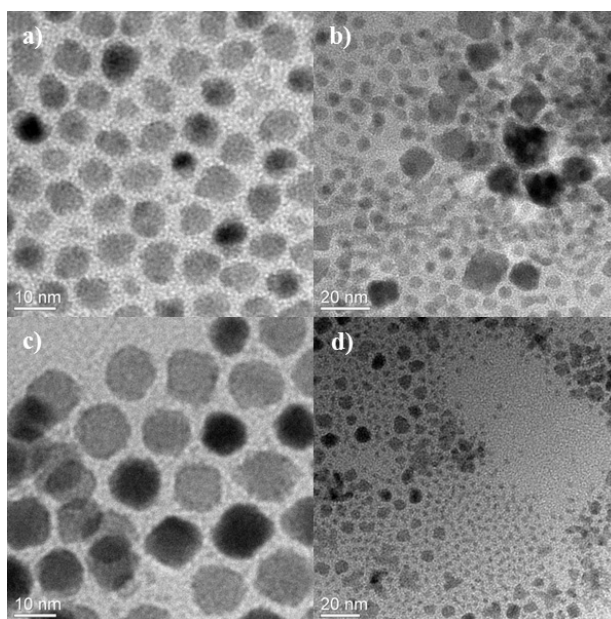


Figure 1. a) PbS NPs as synthesized at 90 °C for 30 minutes; b) PbS NPs as synthesized at 90 °C for 10 minutes; c) PbS NPs as synthesized at 120 °C for 10 minutes; d) PbS NPs as synthesized at 90 °C with Pb:S ratio 4:1 for 10 minutes.

We also studied the effects from doping with transitional metal. Mn acetate was mixed with PbO precursor at 10% and 20% molar ratios in the growth of PbS NPs, and the TEM results show the morphology will be affected as well. As can be seen from Figure 2, 10% Mn growth at

120 °C yields cube-like nanoparticles, while 20% Mn growth at 120 °C yields polyhedron shaped nanoparticles. In both cases, the sizes of nanoparticles are apparently bigger than those without Mn precursor. Further studies by elemental analysis will be needed to determine whether or not the Mn is indeed doped inside the PbS lattice; yet the doping is obviously affecting the morphology as well as sizes of the grown nanoparticles.

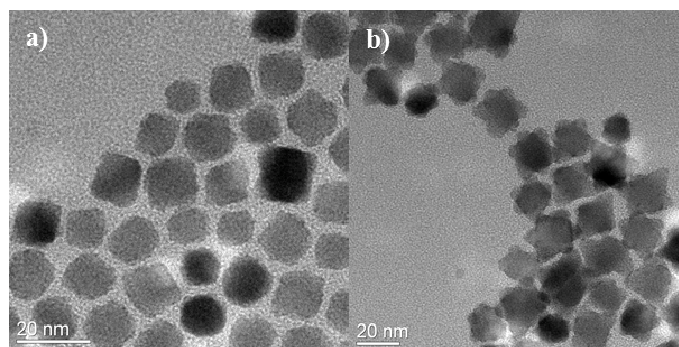


Figure 2. a) PbS NPs grown for 10 minutes with 10% Mn acetate; b) PbS grown for 10 minutes with 20% Mn acetate.

3.2. XRD

The as-synthesized PbS NPs under different conditions were measured by a Rigaku Miniflex II X-Ray diffractometer. XRD is a standard technique to identify materials and reveal impurities.

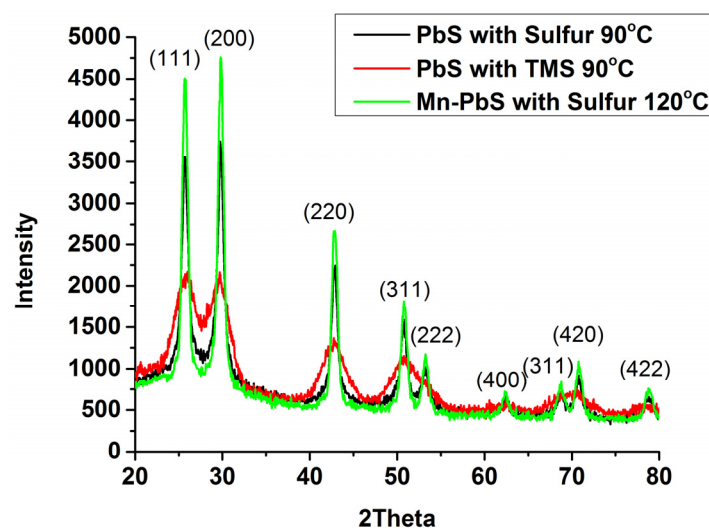


Figure 3. XRD spectra of as-synthesized PbS NPs. The nanoparticles grown by using TMS (red curve) are generally smaller than the nanoparticles grown by sulfur powder (red) at same conditions (temperatures and time) and therefore shows broader XRD peaks. Mn-PbS NPs grown at 120 °C with sulfur powder show narrowest peaks (green curve).

As can be seen from Figure 3, the PbS identification peaks are present without any impurities peaks regardless of the synthesis conditions. However, when the PbS NPs are synthesized with TMS (Bis(trimethylsilyl) sulfide), it shows obviously wider peaks (red curve) as this method tends to give smaller nanoparticles at same temperatures (<3 nm for 90 °C synthesis). The PbS and Mn-PbS synthesized at 90 °C and 120 °C show similar but different peak widths (black and green curves) because of the difference in growth temperatures; the peak positions are not shifted, suggesting the introducing Mn will not affect the lattice structure significantly.

3.3. Absorption Spectra

The as-synthesized nanoparticles were characterized by a Perkin-Elmer Lambda 750 UV-Vis-NIR spectrometer.

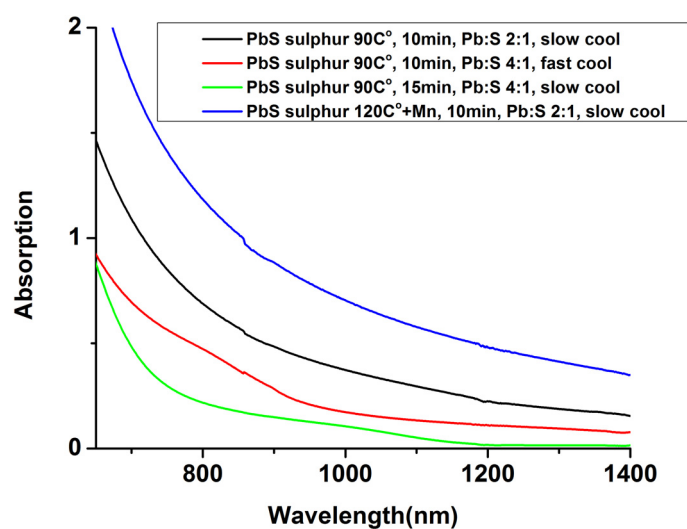


Figure 4. Absorption spectra of synthesized PbS NPs synthesized under different conditions. a) (black curve) PbS NPs synthesized at 90 °C for 10 minutes with Pb:S ~ 2:1 has a characteristic peak around 1150 nm; b) (red curve) PbS NPs synthesized at 90 °C for 10 minutes with Pb:S ~ 4:1 with fast cooling has a characteristic peak around 800 nm; c) (green curve) PbS NPs synthesized at 90 °C for 15 minutes with Pb:S ~ 4:1 with slow cooling has a characteristic peak around 1000 nm; d) PbS NPs with Mn synthesized at 120 °C for 10 minutes with Pb:S ~ 2:1 with slow cooling has no characteristic peak.

As shown in Figure 4, all absorption spectra curves were measured with nanoparticles synthesized at 90 °C except that the last one was synthesized with Mn acetate at 120 °C. We also did fast-cooling in one of the samples to study if it has any effects on the growth. The PbS NPs synthesized with Pb:S ~ 2:1 ratio at 90 °C (black curve) shows a characteristic peak around 1150 nm; the PbS NPs synthesized with Pb:S ~ 4:1 ratio at 90 °C (red curve) with fast cooling (when quenching the synthesis) shows a very weak characteristic peak around 800 nm, while the PbS NPs synthesized with Pb:S ~ 4:1 ratio (green curve) at 90 °C with slow cooling (when quenching the synthesis) shows a characteristic peak around 1000 nm, suggesting continuous growth when

synthesis was quenched slowly; the PbS NPs synthesized with Mn acetate with Pb:S ~ 2:1 ratio at 120 °C (blue curve) shows no characteristic peak. All four curves don't show strong absorption peaks, which can be explained by the low crystallinity caused by sulfur precursor and oleic acid. Mn doping seems to have no effect on the absorption spectra either. Precursor ratio 4:1 tends to produce non-uniform growth with many smaller nanoparticles, as can be confirmed from TEM images in Figure 1d.

4. Conclusion

In this paper, we reported a study of synthesis conditions (such as growth temperatures, growth time, precursor ratio, and quenching) of PbS NPs using sulfur powder as sulfur precursor and oleic acid as stabilizer. We found out the strong correlation between growth conditions and morphology of nanoparticles. Growth at 120 °C generally yields more uniform morphology with sizes more than 10 nm; growth for 10 minutes or less usually gives different morphology in the nanoparticles; introducing Mn precursor affects the morphology as well as the sizes of PbS NPs; quenching the experiment fast or slow will have effects on the absorption peaks; growth conditions such as growth temperature and growth time overall affect only the widths of peaks of the XRD spectra but not the identification peaks (2θ), as no impurities phases are grown. Further studies will be done to reveal the more specific correlations between synthesis conditions and performances of photovoltaic or thermoelectric devices fabricated with them.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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