DE GRUYTER DOI 10.1515/mgmc-2012-0036 — Main Group Met. Chem. 2012; 35(5-6): 173–178

Gholamreza Nabiyouni*, Emad Moghimi, Kambiz Hedayati and Rouhollah Jalajerdi

Room temperature synthesis of lead sulfide nanoparticles

Abstract: Lead sulfide (PbS) nanoparticles were synthesized at room temperature via a simple chemical reaction. In this work, thiophenol was used as the capping agent and sodium sulfide was used as a sulfur source. The products were characterized using X-ray diffraction, scanning electron microscopy, transmission electron microscopy, ultraviolet-visible, photoluminescence and Fourier transform infrared spectroscopy. Electron microscopy studies reveal that synthesis of PbS nanoparticles using no capping agent produces PbS nanoparticles with relatively large size, whereas adding thiophenol leads to the production of nano-sized PbS particles. We found that electronic absorption spectra as well as particle sizes depend on the used capping agents. Compared with bulk PbS, the absorption spectra of the obtained PbS nanoparticles exhibit a blue shift, which can be attributed to the quantum confinement of charge carriers in the nanoparticles.

Keywords: lead sulfide; nanoparticles; thiophenol.

***Corresponding author: Gholamreza Nabiyouni,** Faculty of Science, Department of Physics, Arak University, Arak 38156-8-8349, Iran, e-mail: g-nabiyouni@araku.ac.ir
Emad Moghimi: Department of Physics, Islamic Azad University, Karaj Branch, Karaj, Iran
Kambiz Hedayati: Faculty of Science, Department of Physics, Arak University, Arak 38156-8-8349, Iran
Rouhollah Jalajerdi: Young Researchers Club, Arak Branch, Islamic Azad University, Arak, Iran

Introduction

Nanostructured materials have attracted extraordinary research interest owing to their fundamental significance for addressing some basic issues of the quantum confinement effect. It is expected that the third-order nonlinear optical response of lead sulfide (PbS) nanocrystals is 1000 times larger than that of cadmium selenide. Thus PbS nanocrystals may be considered as a promising candidate for photonic and optical switching devices (Salavati-Niasari et al., 2009, 2010, 2012; Ghanbari et al., 2012; Nabiyouni et al., 2012). Many physical and chemical properties, such as melting point, color and band gap, and electronic properties of materials strongly depend on particle sizes (Ji et al., 2003; Ni et al., 2006; Yousefi et al., 2011; Salavati-Niasari and Ghanbari, 2012). PbS is an important semiconductor material because of its exciton Bohr radius which is 18 nm at room temperature. It is well known that, if the average crystal size of a typical semiconductor is smaller than the Bohr radius, having a small band gap and a large exciton Bohr radius makes it as an interesting system for studying the effect of size confinement. PbS nanoparticles may also be useful in electroluminescent devices such as light-emitting diodes and optical switches (Kuang et al., 2003; Wang et al., 2003; Chakraborty and Moulik, 2005; Lu et al., 2006; Zhang et al., 2006a,b; Zhou et al., 2006). In this work, we introduce an easy chemical route to synthesize PbS nanoparticles with different particle sizes, simply using thiophenol as a capping agent. The PbS nanoparticle size is controlled by the concentration of thiophenol.

Results

X-ray diffraction (XRD) patterns of as-synthesized PbS with 1 M of thiophenol and a standard peak list are shown in Figure 1A and B, respectively. The patterns were indexed as pure cubic phases (galena), which are very close to the literature value (JCPDS No. 02–1431). The crystallite size of PbS was calculated from the XRD pattern using the Scherrer formula.

$$D=\frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where λ is the X-ray wavelength (=1.54 Å), θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) of the peak appearing at the diffraction angles (Nabiyouni et al., 2012). The crystallite size estimated from the Scherrer formula was about 20 nm.

A scanning electron microscopy (SEM) image of the synthesized bulk PbS (without using thiophenol) is shown in Figure 2A. SEM images of PbS with 0.05, 0.1, 0.5 and 1 M of thiophenol are shown in Figure 2B–E, respectively. The images show that the PbS nanocrystals are spherical in shape with an average diameter of < 100 nm which decreases with increasing thiophenol concentration.

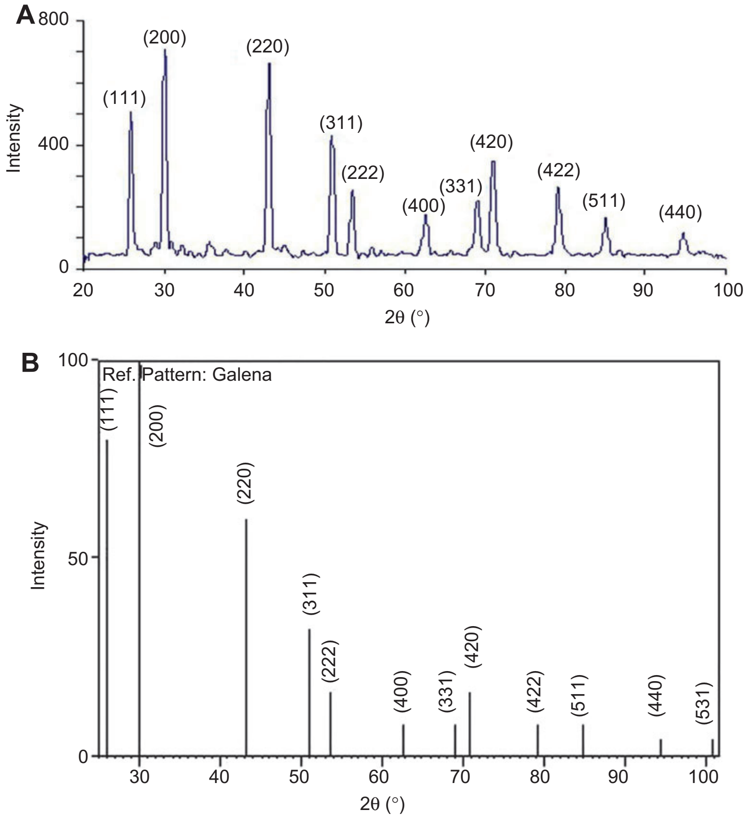

Figure 1 XRD pattern of the (A) obtained PbS with 1 M of thiophenol (B) standard peak list.

Transmission electron microscopy (TEM) images of the PbS nanoparticles with 0.5 and 1 M of thiophenol are shown in Figure 3A and B, respectively. The average particle size, estimated from TEM images, was about 20 nm, which is in agreement with the XRD results. The purity of PbS nanoparticles was also confirmed by energy-dispersive X-ray spectroscopy (EDX) analysis (Figure 4), where the L_a, L_b lines of lead and the K_a and K_b lines of sulfur are obviously observed.

It is well known that changing the semiconductor particle size leads to a shift in semiconductor energy levels. Thus materials with different particle sizes exhibit different band gaps. Usually, a decrease in particle size causes an increase in the band gap and a blue shift occurs (Salavati-Niasari et al., 2009). Figure 5A–D gives the UV-visible electronic absorption spectra of the nanoparticles with 0.05, 0.1, 0.5 and 1 M of thiophenol, respectively. As can be seen from the Figure, adding thiophenol to the solution (as the capping agent) leads to a decrease in PbS particle size and results in the quantum confinement of charge carriers in the nanoparticles, and a large blue shift (compared with the bulk PbS, band gap: 0.4 eV, 3020 nm) is observed (Yousefi et al., 2011). It can also be seen that the peak values of PbS nanoparticles (synthesized with 0.5 and 1 M of thiophenol) are smaller than those observed from the absorption spectra of the sample synthesized with concentrations of 0.05 and 0.1 M of thiophenol, indicating that the latter have a smaller size than the former, in agreement with our previous work (Nabiyouni et al., 2012).

Photoluminescence (PL) measurement of the PbS nanoparticles obtained with 1 M of thiophenol at room temperature with an excitation wavelength of 362 nm is shown in Figure 6. The PL spectrum consisted of a strong peak at 421 nm that can be ascribed to a high level of transition in PbS semiconductor crystallites. It has been reported that this kind of band edge luminescence arises from the recombination of excitons and/or shallowly trapped electron-hole pairs (Salavati-Niasari et al., 2012).

The Fourier transform infrared (FT-IR) of the PbS nanoparticles obtained with 0.05, 0.1, 0.5 and 1 M of thiophenol are shown in Figure 7A–D, respectively. FT-IR spectroscopy shows the presence of small amounts of thiophenol adsorbed on the PbS surface.

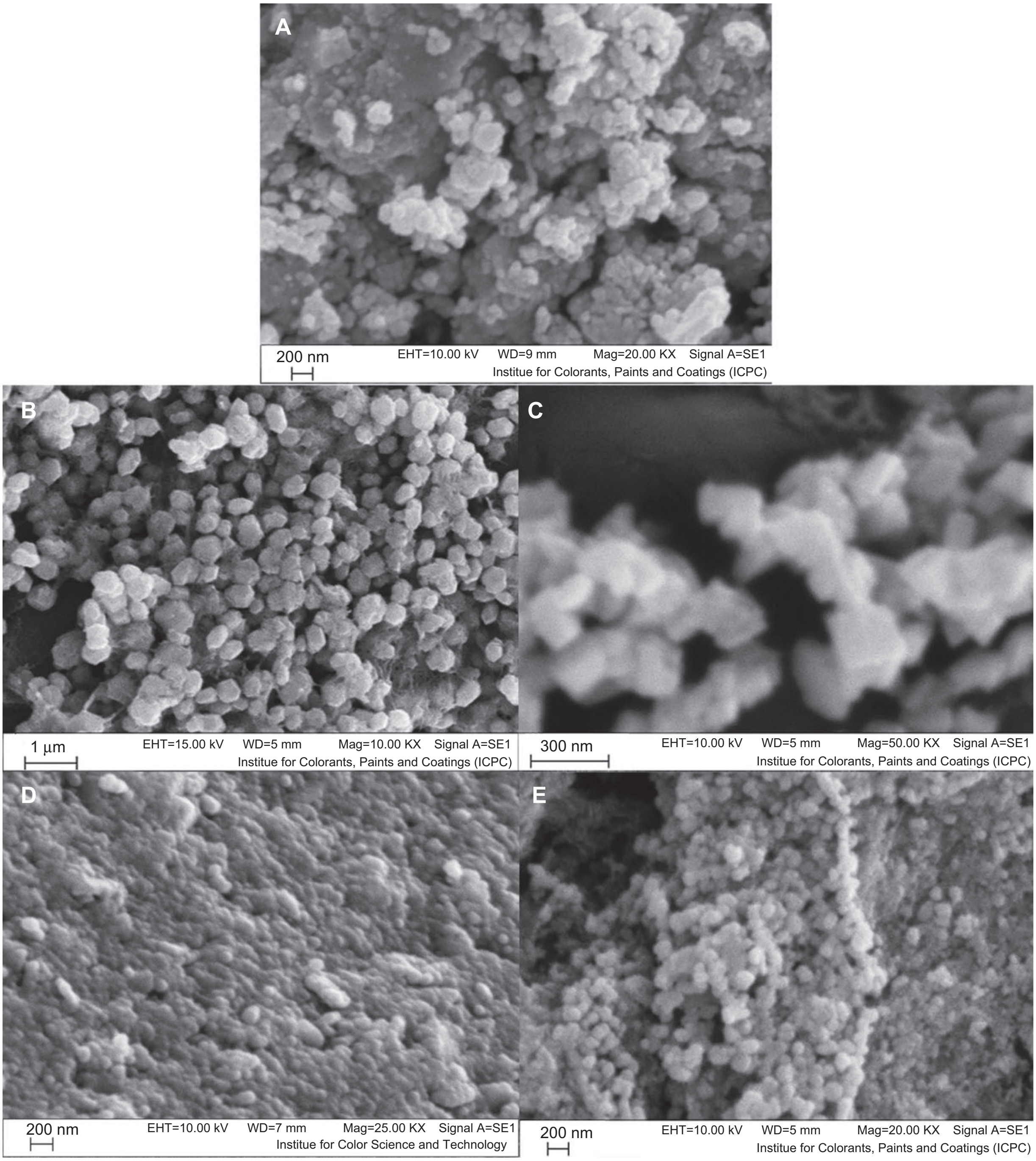

Figure 2 SEM images of the PbS nanocrystals synthesized (A) without thiophenol and with (B) 0.05, (C) 0.1, (D) 0.5 and (E) 1 M of thiophenol.

Absorption peaks at 1440 and 1600 cm^{-1} are attributed to the stretching vibration of aromatic ring, and a peak at 3025 cm^{-1} is responsible for the aromatic C–H bond, and an absorption peak at 1106 cm^{-1} is due to the C–O bond.

Conclusions

Lead sulfide nanoparticles were synthesized at room temperature via a simple chemical reaction. In this synthesis, thiophenol was used as the capping agent and

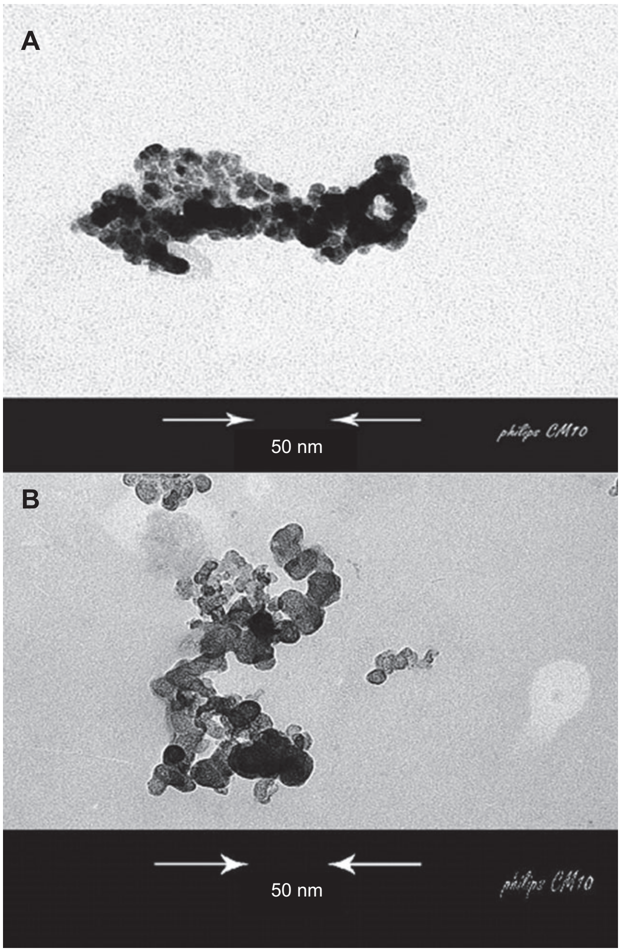

Figure 3 TEM images of the PbS nanoparticles synthesized with (A) 0.5 and (B) 1 M of thiophenol.

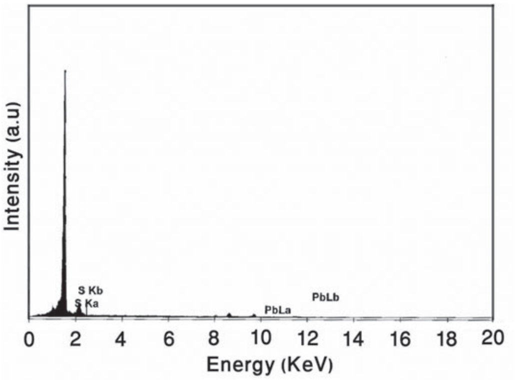

Figure 4 EDX pattern of the PbS nanocrystals synthesized with 1 M of thiophenol.

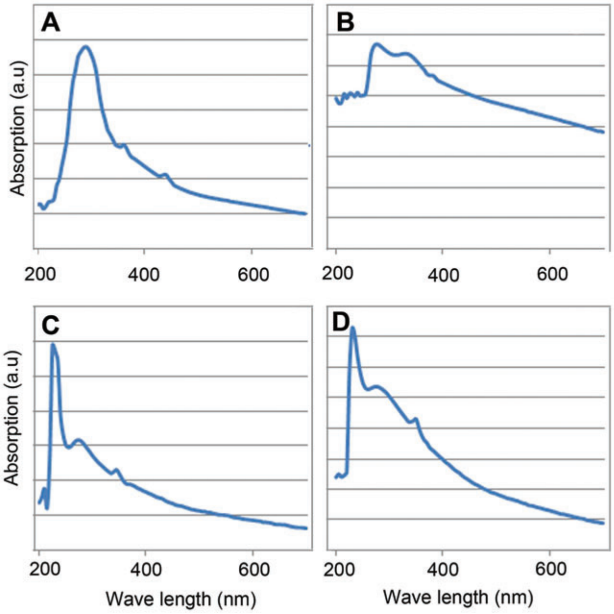

Figure 5 UV-Visible absorption spectra of the PbS nanocrystals synthesized with (A) 0.05, (B) 0.1, (C) 0.5 and (D) 1 M of thiophenol.

sodium sulfide was used as a sulfur source. SEM images show that, without using a capping agent, bulk PbS is obtained, whereas adding thiophenol leads to the production of nanoparticles. Compared with bulk PbS, which has a band gap of 3020 nm, absorption of the obtained PbS nanostructures exhibits a large blue shift, which is attributed to the quantum confinement of charge carriers in the nanostructures. The average particle size, estimated from the TEM images, was about 20 nm.

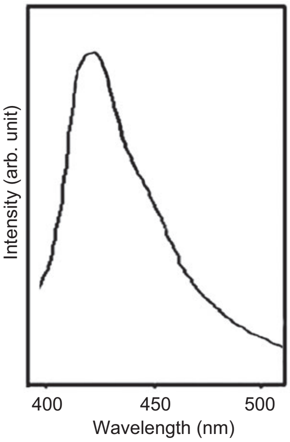

Figure 6 Room temperature photoluminescence spectrum of the obtained PbS with 1 M of thiophenol.

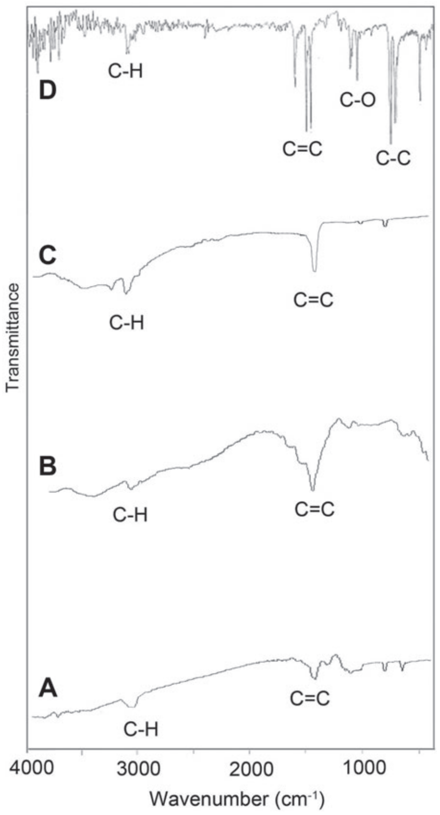

Figure 7 FT-IR spectrum of the obtained PbS with (A) 0.05, (B) 0.1, (C) 0.5 and (D) 1 M of thiophenol.

Experimental

Materials and physical measurements

Thiophenol, lead nitrate and sodium sulfide were of analytical grade from Merck & Co, Inc. X-ray diffraction (Philips PW3373, Netherlands) with CuK_α (λ=1.54 Å) radiation was used for structural characterization. SEM images were obtained using a LEO 1455VP scanning electron microscope (UK). Prior to taking images, the samples were coated with a very thin layer of Au to make the sample surface conductive, prevent charge accumulation and obtain a better contrast. Nanoparticle size was measured using a Philips CM 200 FEG transmission electron microscope (Netherlands). The UV-visible absorption spectra were taken using a Scinco SUV-2120 UV-visible spectrophotototometer (Korea). FT-IR spectrum was recorded on a Galaxy series FTIR 5000 spectrophotometer (UK).

Synthesis of PbS nanoparticles

A total of 0.05 g of $Pb(NO_3)_2$ was dissolved in 25 ml of deionized water. Twenty-five milliliters of thiophenol with different concentrations (0.05, 0.1, 0.5 and 1 M) was then slowly added to the $Pb(NO_3)_2$ solution under nitrogen atmosphere. Finally, 25 ml of 0.01 M aqueous solution of Na_2S was added to the above solution. The color of the final transparent colloidal suspensions went from light brown to black by adding thiophenol with different concentrations. The color of the final suspensions went from brown to black by adding thiophenol with different concentrations.

References

Chakraborty, I.; Moulik, S. P. On PbS nanoparticles formed in the compartments of water/AOT/*n*-heptane microemulsion. *J. Nanopart. Res*. **2005**, *7*, 237–247.

Ghanbari, D.; Salavati-Niasari, M.; Davar, F. Synthesis of different morphologies of PbS nanostructures via hydrothermal process. *High. Temp. Mater. Proc*. **2012**, in press. DOI:10.1515/htmp-2012–0152.

Ji, Y.; Ma, X.; Zhang, H.; Xu, J.; Yang, D. Star-shaped PbS crystals fabricated by a novel hydrothermal method. *J. Phys. Condens. Mat*. **2003**, *15*, 7611–7615.

Kuang, D. B.; Xu, A. W.; Fang, Y. P.; Liu, H. Q.; Frommen, C.; Fenske, D. Surfactant assisted growth of novel dendritic nanostructures via facile hydrothermal process. *Adv. Mater*. **2003**, *15*, 1747–1750.

Lu, Q.; Gao, F.; Komarneni, S. Multi-level assemblies of lead sulphide nanorods. *Nanotechnology*. **2006**, *17*, 2574–2580.

Nabiyouni, G.; Boroojerdian, P.; Hedayati, K.; Ghanbari, D. A simple method for synthesis of PbS nanoparticles using 2-mercaptoethanol as the capping agent. *High Temp. Mater. Proc*. **2012**, in press. DOI: 10.1515/htmp-2012–0155.

Ni, Y.; Wei1, X.; Hong, J.; Ma, X. PbS microcrystals with a magic-square-like structure prepared by a simple hydrothermal method. *Cryst. Res. Technol*. **2006**, *41*, 885–888.

Salavati-Niasari, M.; Ghanbari, D. Hydrothermal synthesis of star-like and dendritic PbS nanoparticles from new precursors. *Particuology* **2012**, *10*, 628–633.

Salavati-Niasari, M.; Ghanbari, D.; Davar, F. Synthesis of different morphologies of bismuth sulfide nanostructures via hydrothermal process in the presence of thioglycolic acid. *J. Alloy. Compd*. **2009**, *488*, 442–447.

Salavati-Niasari, M.; Ghanbari, D.; Davar, F. Shape selective hydrothermal synthesis of tin sulfide nanoflowers based on nanosheets in the presence of thioglycolic acid. *J. Alloy. Compd*. **2010**, *492*, 570–575.

Salavati-Niasari, M.; Ghanbari, D.; Loghman-Estarki, M. R. Star-shaped PbS nanocrystals prepared by hydrothermal process in the presence of thioglycolic acid. *Polyhedron*. **2012**, *35*, 149–153.

Wang, D.; Yu, D.; Shao, M.; Liu, X.; Yu, W.; Qian, Y. Dendritic growth of PbS crystals with different morphologies. *J. Cryst. Growth*. **2003**, *257*, 384–389.

Yousefi, M.; Gholamian, F.; Ghanbari, D.; Salavati-Niasari, M. Polymeric nanocomposite materials: Preparation and characterization of star-shaped PbS nanocrystals and their influence on the thermal stability of acrylonitrile-butadiene-styrene (ABS) copolymer. *Polyhedron*. **2011**, *30*, 1055–1060.

Zhang, H.; Zuo, M.; Tan, S.; Li, G.; Zhang, S. Carbothermal reduction/sulfidation synthesis and structural characterization of PbS nanobelts and nanowires. *Nanotechnology*. **2006a**, *17*, 2931.

Zhang, Z.; Lee, S. H.; Vittal, J. J.; Chin, W.S. A simple way to prepare PbS nanocrystals with morphology tuning at room temperature. *J. Phys. Chem. B*. **2006b**, *110*, 6649–6654.

Zhou, G.; Lu, M.; Xiu, Z.; Wang, S.; Zhang, H.; Zhou, Y.; Wang, S. Controlled synthesis of high-quality PbS star-shaped dendrites, multipods, truncated nanocubes, and nanocubes and their shape evolution process. *Phys. Chem. B*. **2006**, *110*, 6543–6548.