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A CONVENTIONAL SYNTHESIS APPROACH TO PREPARE LEAD SULFIDE (PbS) NANOPARTICLES VIA SOLVOTHERMAL METHOD

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We are describing a new optimized method for the preparation of single-sized crystalline lead sulphide (PbS) nanoparticles (NPs). The optimized solvothermal method uses a mixture of octadecene and oleic acid as a reaction media and MBTS as a reducing agent. Systematic investigation was performed on various synthesis parameters, such as acid to lead (Pb) and lead to sulphur(S) feed molar ratios, feed amounts of various phosphine compounds, reducing agent, total concentrations of reaction media, growth temperature, as well as different sulphur source compounds. We optimized the amount of 2,2-dithiobis(benzothiazole) (MBTS) in the reaction mixture to produce about 100 nm size and spherical shape zinc blade type PbS NPs. A broad UV absorption spectrum was observed when the MBTS amount was increased in the reaction mixture. The excellent organic solvent dispersion properties, along with near-IR emission spectrum window make these NPs a great choice in optoelectronics applications, especially for photovoltaic devices.

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1. Introduction

Lead sulphide (PbS) nanoparticles (NPs), together with other lead chalcogenides including PbSe and PbTe have demonstrated to be the most promising candidates for photovoltaic (PV) devices. PV devices fabricated with lead salts often perform well with relatively high power conversion efficiency (PCE), e.g., colloidal PbS NPs based devices have reached a PCE value of 1.8%;[1]significant efforts are still on-going with the lead chalcogenide NPs targeting even higher PCEs.[2]

Currently, the preparation of high quality PbS materials utilizes lead oxide and Bis(trimethylsilyl) sulphide [$(TMS)_2S$] as the starting materials,[1,3-7]which are expensive, air-sensitive and extremely toxic. The involvement of $(TMS)_2S$ not only endures high-cost, but also requires careful chemical-handling in glove-box or special facilities due to the toxic nature of this chemical. In addition, the widely used synthetic method[3-9]utilizesa typical wet chemistry technique, which is known to limit the scale of material production. The large-scale production of PbS NPs is required if PbS based PVs devices come to commercialization. This would significantly elevate the manufacturing cost, considering the high-cost of the raw materials, the air-sensitive chemicals handlings and the low-scale production capability of single batch reactions. Therefore, there is an

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urgent need to develop a synthetic protocol that produces a high quality PbS nanocrystals with the capacity for large-scale production, by using a greener and less expensive precursors material. The new methodology is needed to keep or even further promote the momentum of the currently intensive studies of PVs by using colloidal PbS NPs. After a comprehensive screening of approaches for the synthesis of PbS NPs, we developed a methodology that has the potential for a large-scale production. This was possible by using hydrothermal/solvothermal routes which can simply replace non-injection wet-chemistry approaches.[5,6] Moreover, all the precursors are greener compound and stable in air, thus does not require any special handling tools.

In this article, we report a simple solvothermal method using an inexpensive precursor source compounds to produce "single-crystals of PbS" NPs. The product "single-crystals of PbS" NPs have been characterised using transmission electron microscopy (TEM) and X-ray diffraction (XRD).The produced NPs were highly crystalline and have better solution process ability. This study will represent a big step forward on the journey to "low-cost" and "high-reproducibility" of PbS NPs for PV devices. We also investigated various synthetic parameters, such as Acid/Pb and Pb/S feed molar ratios, and feed amounts of various phosphine compounds, reducing agent, total concentrations of reaction media, and growth temperature, as well as different Pb and S source compounds of synthetic parameter in sequence. Various PbS NPs ensembles of different sizes can be engineered from one synthetic batch. We found that the growth temperature rather than growth period controls the NPs size. Accordingly, this solvothermal synthesis features easy handling with high reproducibility and scale-up capability for high production yield.

2. Experimental details

2.1 Materials

All the chemicals (unless mentioned otherwise) were purchased from Aldrichand were used as received. (i) Pb source compounds: Lead oxide (PbO, 99.9%), (ii) Two S source compounds: elemental sulphur (Anachemia, powder) and thioacetamide (TAA, 99.0%), (iii) Acid: oleic acid (OA, tech. 90%) (iv) Three Phosphines: tributylphosphine (TBP, 97%), trioctylphosphine (TOP, 90%) and Di-phenlyphosphine (DPP, 98%), and (v) reducing agent 2,2'-dithiobisbenzothiazole (MBTS, 99%).

2.2 Typical Synthesis of PbSNPs.

PbS NPs synthesis process was divided into three steps. Firstly: (*Pb-stock solution preparation*), PbO, OA, and ODE were loaded in a 50 mL three-neck reaction flask at room temperature. After degassing, the mixture was heated to 120ºC while stirring under vacuum for one hour to form a clear precursor of lead oleate (Pb(OA)2) and subsequently cooled to ambient temperature. Secondly: (*S-Stock solution preparation*), elemental S or TAA (thioacetamide, CH_3CSNH_2) was sonicated with ODE for 1 hour to control the room temperature to form an S source milk solution in vials. These two stock solutions can be preserved under nitrogen atmosphere in sealed vials and used when necessary. Finally, a mixture of the stoichiometric amount of Pb-stock solution, S-stock solution, ODE and the reducing agent (benzothiazoledisulfide (2.2'-Dithio-dibenzothiazole) (MBTS)) were transferred to the Taflon-lined autoclave. The NPs growth was later carried out at either room temperature or elevated temperature. The mixture was heated up at a constant rate of 10ºC/minute, followed by an isothermal stage at 50°C, 80°C, 100°C, and 120°C for 30 to 60 minutes and subsequently quenched to the ambient temperature. Afterwards, 30 μL of each sample was dispersed into 3 mL toluene for the measurement of the optical properties of the growing PbS ensemble. Absorption spectra were collected on UV-3600 UV/Vis/NIR spectrometer (Shimadzu, Japan) using a 1-nm data collection interval and scan rate of 600 nm/min, Photoemission experiments were performed on a RF-5301PC spectrometer (Shimadzu, Japan), with a 450 W Xe lamp as the excitation source, an excitation wavelength of 500 nm (if not specified), an increment of data collection of 2 nm, and the slits for excitation and emission of 3 nm. If necessary, aliquots were purified by precipitation twice in toluene/methanol; and the purified powders were dispersed in toluene with a proper concentration.

2.3 Synthesis of single-sized, ~100 nm PbS nano-materials.

After the mixing of the S-stock into the Pb-stock with a reducing agent (benzothiazoledisulfide (2.2'-Dithio-dibenzothiazole) (MBTS)) in feed molar ratio (4:1:1) in the Teflon-lined autoclave, stainless chamber was screwed well with lid and placed in an oven. Then, the oven was heated up by a rate of ca 10°C/min from room temperature to 100ºC. Growth temperature 100°C for a duration of 60 minutes was used to acquire the desired ~100 nm PbS NPs. Afterward, 50 µL of each sample was dispersed into 3 mL of toluene for the measurement of the optical properties of the growing PbS ensemble.

2.4 PbS NPs purification for XRD and TEM measurements

A mixture of toluene and methanol was added into as-synthesized PbS NPs to precipitate the nanoparticles. After centrifugation (4000rpm for 10 minutes), the supernatant was decanted and toluene was added, and PbS NPs were dispersed with gentle shaking. The purification process was carried out for three times. For TEM characterization, a purified sample stored in toluene was deposited on a carbon-coated copper grid and was analysed by JEM-2100F (JEOL, Japan) electron microscope operating at 200 kV and equipped with a Gatan UltraScan 1000 CCD camera. Powder XRD patterns were recorded at room temperature on a XRD-7000 (Shimadzu, Japan) X-ray diffractometer using Cu Kα radiation in a θ - θ mode. The generator was operated at 40 kV and 40 mA, and data were collected between 5° and 80° in 2θ with a step size of 0.1° and a counting time of 5 s per step. XRD samples were prepared by depositing the purified nanoparticles on a low-background quartz plates.

3. Results and discussions

This article addresses solvothermal synthetic method and low-temperature approach for large-scale production of crystalline "single-crystal-size" PbS NPs in ODE solvent. The first part investigates the various synthesis parameters, including acid-to-Pb-to-S feed molar ratios, reaction temperature, treatment time, with and without reducing agents, different S source compounds etc. In the discussion section, we examine the characterization of the produced NPs using the absorption spectrum from each batch of reaction. Finally, we will also discuss the structure and characterization of PbS NPs by XRD and TEM. We only tested the most conveniently prepared PbS crystals with controllable size and morphology with this method.

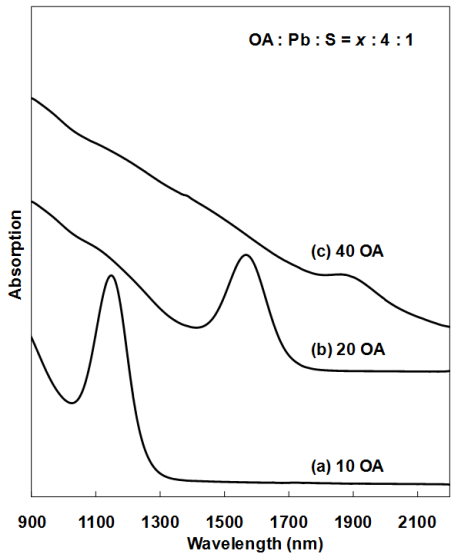

Fig. 1. Absorption spectra from three different batches (a) 10, (b) 20, (c) 40 feed molar ratio of oleic acid. Each reaction carried out at constant parameters of (i) feed molar ratios Pb : S = 4 : 1, (ii) concentration [S] = 50 mmol/Kg, (iii) reaction time 30 minutes and (iv) reaction temperature 100℃.

The preparation of PbS NPs by solvothermal synthesis approach is incredibly significant and technologically valuable. With the typical synthetic condition, the acid-to-Pb feed molar ratios have a strong influence on the formation of PbS NPs. The amount of oleic acid (OA) plays an important role affecting the solubility of the resulting PbS NPs in the reaction medium. The amount of OA used will also affect the PbS nanocrystals solubility. Lead oxide precursor was not able to dissolve completely in the form of lead oleate in ODE when the feed molar ratio between Acid : PbO was smaller than 2:1. An excess of two feed molar ratios of acid was used, which means 2.5OA-to-1Pb was preferred to synthesize PbS NPs ensembles with narrow size distribution and tuneable sizes from one synthetic batch. Fig.1 shows the absorption peak positions of the resulting PbS nanocrystals at different molar ratio of oleic acid from the three synthetic batches.

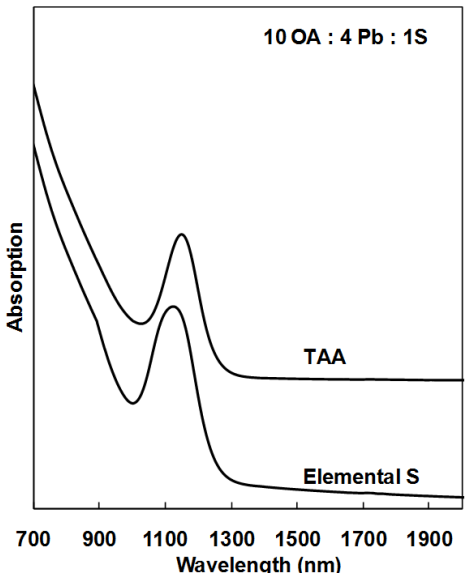

Fig. 2. Absorption spectra from two different batches using TAA and elemental S. Each reaction carried out at constant parameters of (i) feed molar ratios OA :Pb : S = 10: 4 : 1, (ii) concentration [S] = 50 mmol/Kg, (iii) reaction time 30 minutes and (iv) reaction temperature 100°C.

We also tested two sulfur sources, thioacetamide (TAA), and elemental S to synthesize PbS NPs as shown in Figure 2. TAA has often been used to synthesize PbS NPs with various morphologies in aqueous media.[10,11] With elemental S as the S source, 2,2-dithiobis(benzothiazole) (MBTS) was used together to enhance S reactivity.[12] Using the typical synthesis condition with two different S precursors, several reaction batches were prepared under the same reaction condition: feed molar ratios of OA : Pb : S = 10 : 4 : 1 with the growth temperature increasing from 50ºC up to 120°C and reaction time of 30 min. The temporal evolution of the absorption spectra reveals that the two S precursor compounds have different reactivity with the TAA having higher reactivity than elemental S. The formation of PbS NPs started at 50°C with TAA, whereas similar good absorption spectrum was observed when elemental S including MBTS was used as reducing agent at100°C.However, the PbS NPs produced from elemental S exhibited poor photoluminescence spectra. With the use of only elemental S, and a temperature higher than 100°C, PbS NPs with very broad absorption spectrum were obtained with no photoluminescence at all.

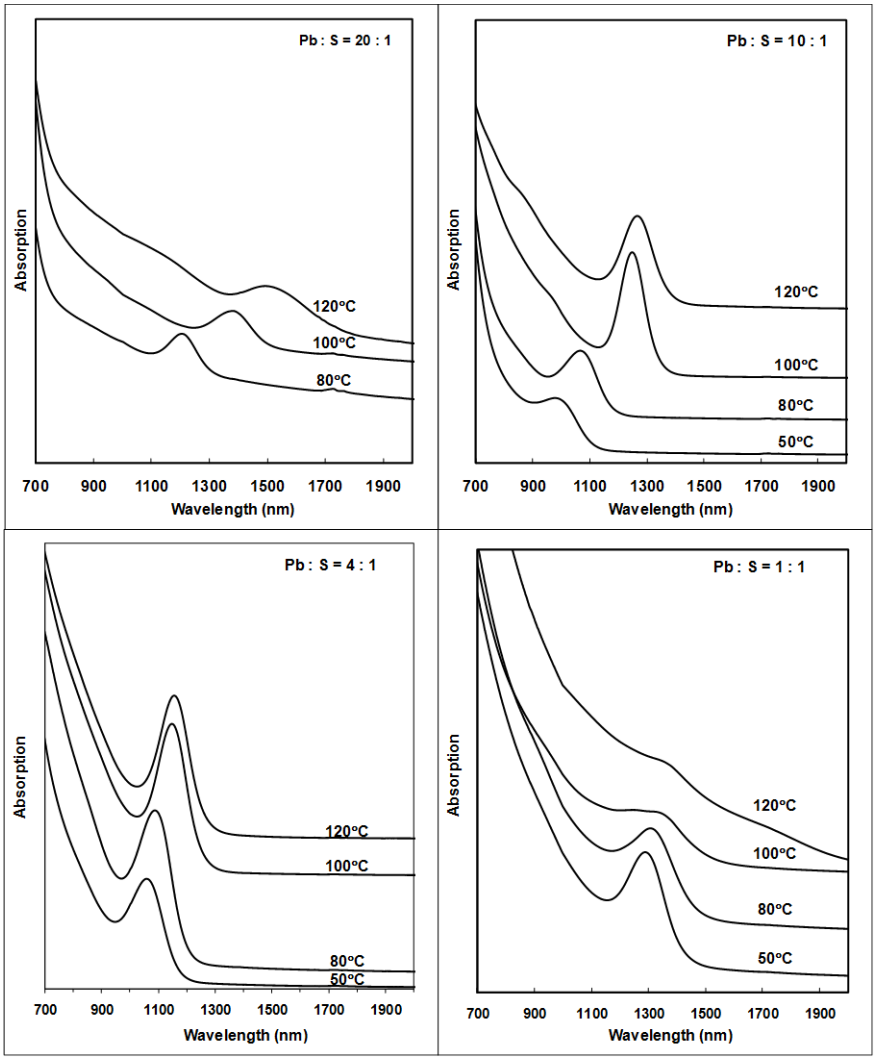

Fig. 3.Absorption spectra from fifteen different batches. Each reaction carried out at (a) 50°C, (b) 80°C, (c) 100°C, (d) and 120°C, and fixed parameters are (i) concentration [S] = 50 mmol/Kg and (ii) reaction time 30 minutes.

After considering the amount of acid and the precursor of S, Pb to S feed molar ratios of 20Pb-1S, 10Pb-1S, 4Pb-1S and 1Pb-1S using the typical synthetic conditions were further investigated. Figure 3 shows the temporal evolution of the absorption spectra of the growing nanocrystals from fifteen different batches with the typical synthesis procedure mentioned in the experimental section, where feed molar ratios of Pb varies from 20-to-1 with 1 limited S. After the mixing of the Pb-precursor and S-precursor solutions at room temperature, the colour of the solution changed from clear yellow to brown, and then black, indicating the presence of a nucleation/growth process of PbS NPs. With a Pb : S feed molar ratio of 20 : 1 , the nanocrystals grow too fast, while a molar ratio of 1 : 1 exhibited slower growth rate. The peak positions of the bandgap absorption shifted in shorter wavelength region with increasing the feed molar ratio of Pb : S due to the decrease of the PbS NPs size. We also observed that in each of the feed molar ratios, the peak positions of the bandgap absorption shifted in longer wavelength region with increasing of the reaction temperature.

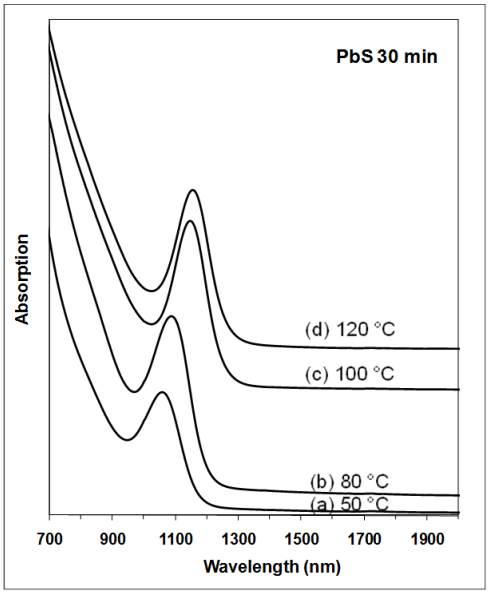

Fig. 4.Absorption spectra from four different batches. Each reaction carried out at (a) 50ºC, (b) 80ºC, (c) 100ºC, (d) and 120ºC, and fixed parameters are (i) feed molar ratios OA : Pb : S = 10 : 4 : 1, (ii) concentration [S] = 50 mmol/Kg and (iii) reaction time 30 minutes.

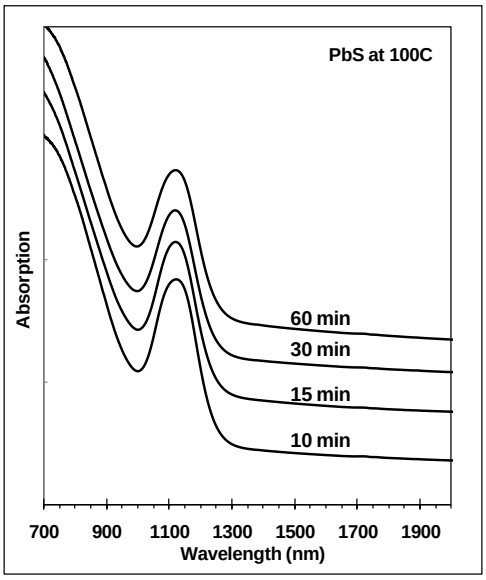

Fig. 5. Absorption spectra from five different batches. Each reaction carried out at 10 min, 15 min, 30 min 60 min, and fixed parameters are (i) feed molar ratios OA : Pb : S = 10 : 4 : 1, (ii) concentration [S] = 50 mmol/Kg and (iii) reaction temperature 100ºC.

Fig. 4(a) shows the temporal evolution of the absorption of the growing NPs with the growth temperature kept at 50 ºC, while Fig. 4(b), Fig. 4(c) and Fig. 4(d) show the same at 80 ºC, 100ºC and 120 ºC, respectively. During the growth periods monitored up to 30 minutes, the first excitonic absorption peaks exhibit relatively large red-shifts for the NPs from the batch with 80 ºC and 100 ºC growths, as compared to that from the batch with 100ºC and 120ºC growth. The lower temperature can give a smaller size of NPs at the beginning of the growth period; however, this mild temperature in spectrum (b) continues to grow at later growth period, corresponding to the absorption peak position at 1090 nm. Spectrum (c) shows the temporal evolution of the absorption of the growing

NPs from the batch with 100ºC growth. As the period increases, the growth ensued to PbS NPs exhibited bandgap absorption with a small red-shift from 1090 nm to 1150 nm; the relatively small red-shift indicates unapparent growth in size of the PbS NPs. This can be explained that the higher temperature lead to a higher reaction rate to supply a large number of nuclei at the beginning growth of period. The sources were almost consumed in nucleation stage and subsequently limited the development of growth. Moreover, each NP ensemble sampled at 100ºC exhibits a single absorption peak with a high symmetry which suggests narrow size distribution. The Pb-precursor and S-precursor solutions are loaded to the taflon container at room temperature. At this stage, the resulting solution changed the colour of the reaction mixture, indicating the presence of a nucleation/growth process of PbS NPs. The oven is preheated to 100ºC, and the sealed stainless-steel vessel is placed and closed the lit of oven. **Fig. 5** shows the temporal evolution of the absorption spectrum of the growing nano-crystals from four different batches with the typical synthesis procedure mentioned in experimental section, where feed molar ratios of the OA : Pb : S = 10 : 4 : 1 and concentration [S] = 50 mmol/Kg and reaction temperature 100ºC are kept constant. Interestingly, all the absorption peak positions were observed at ~ 1120 nm region.

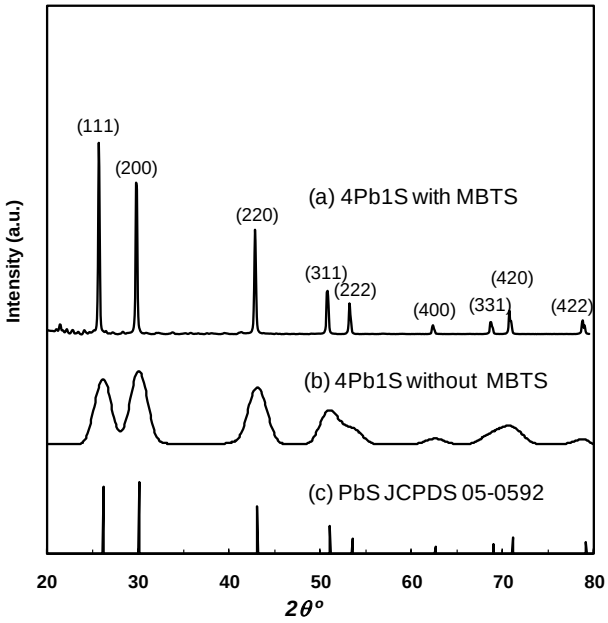

Fig. 6. X-ray diffraction (XRD) patterns of PbS prepared by a solvothermal reaction. (a) with reducing agent, MBTS (b) without reducing agent, MBTS and (c) corresponded with the JCPDS database no. 05-0592 for cubic PbS

Fig. 6 shows the thin-film powder XRD patterns of the 100°C and 60 min growth of PbS NPs with MSTB (Fig. 6a), without MSTB (Fig. 6b) and the corresponding JCPDS database no. 05-0592 for cubic PbS (Fig. 6c).[13] The reflection peaks of (111), (200), (220), (311), (222), (400), (331), (420) and (422) were clearly distinguished, and all these diffraction peaks can be perfectly indexed to a cubic PbS structure with a lattice parameter of a = 5.9362 Å. The strong and narrow peaks indicated a highly crystallinity of the PbS NPs sample, whereas broader peaks appeared from small size crystalline PbS NPs sample. The crystal sizes of several samples were calculated using Scherrer's equation,[14] $B = \lambda k/L\cos\Theta$, where λ is the wavelength of Cu Kα radiation (0.15406 nm),Θ the Bragg angle, L the average crystal size, k a constant (k = 0.89), and B the full width at half maximum (FWHM) in radian unit. The NPs sizes were estimated to be from 10~30 nm by using this Scherrer Equation with the FWHM of the diffraction peak (220). The highly crystalline single-crystal-size, ~100 nm PbS NPs products were characterized by TEM analysis. It should be noted that the crystalline degree and crystallite size of the products were influenced by the prolonged holding time and the high temperature increase.

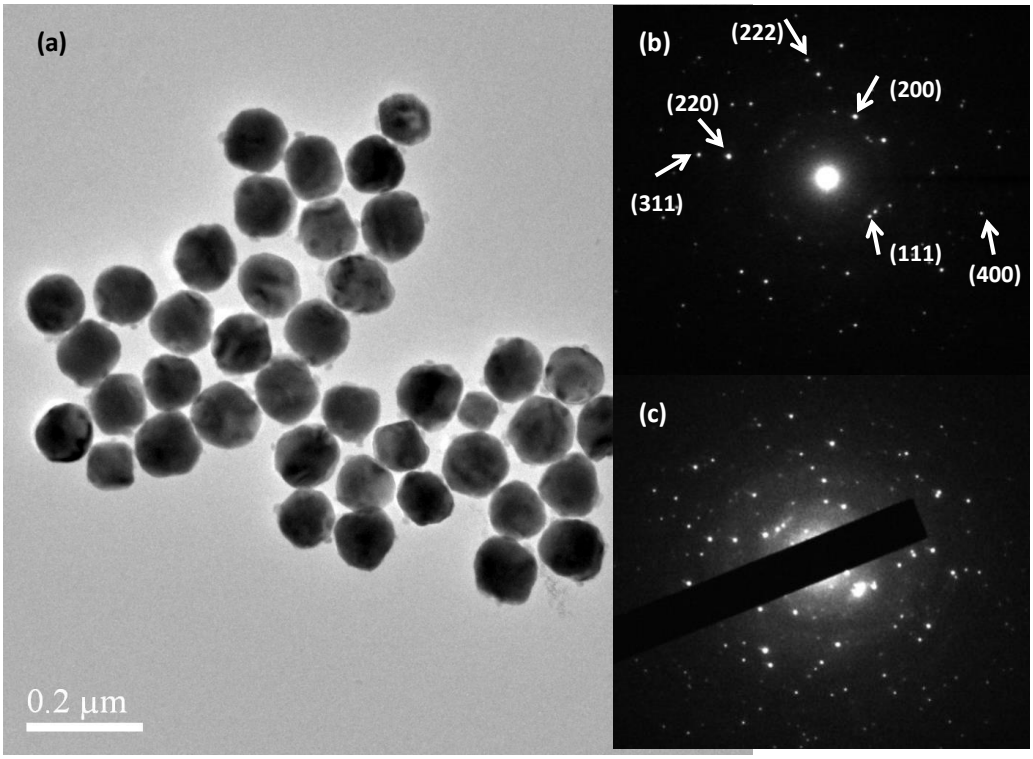

Fig. 7. (a) TEM image (b) and (c) SAED patterns of single-crystal PbS NPs, prepared by the 100ºC and 60 minutes solvothermal method.

The morphologies and size of the prepared PbS NPs were examined by transmission electron microscope (TEM). Optimization of solvothermal treatment (reaction condition: feed molar ratio of OA : Pb : S : MBTS = 10 : 4 : 1 : 1, reaction temperature 100ºC, reaction time 60 min, concentration of S = 50 mmol/kg) were produced an average size of ca 100 nm and spherical shaped PbS NCs. The TEM image and SAED pattern of 100 nm single-size crystalline PbS NPs prepared by the solvothermal method at are shown in Figure 7(a). The SAED pattern shows a number of randomly and continuously bright spots, which are so close that they formed several fully concentric rings. These indicates that the product was consisted of nano-sized crystals with different orientations. Calculated interplanar spaces were compared with those of the JCPDS database no. 05-0592.[13] They correspond to the (111), (200), (220), (311), (222), (400) and (331) planes of the cubic PbS structure.

4. Conclusion

In this article, we developed a low-cost and high reproducibility solvothermal method to synthesize a single-size crystalline PbS NPs. The new method features an easy way of handling chemicals and avoids using air-sensitive organometallic reagents and glass wears. This approach leads to a larger PbS NPs with bandgap in the range of 1100 – 2000 nm and narrow bandwidth. Systematic investigation was performed on the synthetic parameters affecting the formation of PbS NPs. Overall, various reaction conditions and the interplay within play a crucial roles leading to a high-quality crystalline PbS NPs products. We investigated various synthetic parameters, such as Acid to Pb and Pb to S feed molar ratios, and feed amounts of various phosphine compounds, reducing agent, total concentrations of reaction media, and growth temperature, as well as different S source compounds of synthetic parameter in sequence. Additionally, various PbS NPs ensembles of different sizes can be engineered from one synthetic batch. We concluded that the growth temperature rather than growth period mainly controls the NPs size.

Acknowledgements

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References

[1] K. W.Johnston, A. G.Pattantyus-Abraham, J. P.Clifford, S. H.Myrskog, D. D.MacNeil, L.Levina, E. H.Sargent, Applied Physics Letters, **92**,151115(2008).
[2] Quantum dots Thin Film Solar Cells, Patent No. US 0288345 A1, Date of Patent Nov **18**, (2010).
[3] M. A.Hines, G. D. Scholes, Advanced Materials,**15**, 1844, (2003).
[4] Synthesis of Colloidal PbSNanocrystals with Size Tunable NIR Emission, Patent No. US 7118627 B2, Date of Patent Oct 10, (2006).
[5] T-Y.Liu, M.Li, J.Ouyang, Md. B.Zaman, R.Wang, X.Wu, C-S.Yeh, Q.Quan Lin B.Yang, K Yu,,Journal of Physical Chemistry C , **113**, 2301 (2009).
[6] F. Li, Q. Qin, J. Wu, Z Li, Journal of Materials Science, **45**, 348 (2010).
[7] C. Zhang, Z. Kang, E. Shen, E. Wang, L. Gao, F. Luo, C. Tian, C. Wang, Y.Lan, J. Li, X. Cao, Journal of Physical Chemistry B,**110**, 184, (2006).
[8] J. M. Luther, M. Law, M. C. Beard, Q. Song, M. O. Reese, R. J. Ellingson and A. J. Nozik, Nano Letters, **8**, 3488, (2008).
[9] W.Ma, J. M.Luther, H. M.Zheng, Y.Wu, A. P. Alivisatos, Nano Letters, **9**, 1699 (2009).
[10] Z.-P.Qiao, Y.Zhang, L.-T.Zhou, Q. Xire, Crystal Growth & Design, **7**, 2394 (2007).
[11] Y.Ding, X.Liu, R. Guo, Journal of Crystal Growth, **307**, 145 (2007).
[12] J.Ouyang, C. I.Ratcliffe, D.Kingston, B.Wilkinson, J.Kuijper, X.Wu, J. A.Ripmeester, K. Yu, Journal of Physical Chemistry C , **112**, 4908, (2008).
[13] Powder Diffract. File, JCPDS International Centre for Diffracion Data, PA 19073–3273, U.S.A (2001).
[14] C. Suryanarayana, M. G. Norton, "X-ray Diffraction: A Practical Approach", Plenum Press, New York, (1998).