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One-Pot Synthesis of Lead Sulfide Nanoparticles

N. S. Kozhevnikova, S. I. Sadovnikov, and A. A. Rempel'

Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences,
ul. Pervomaiskaya 91, Yekaterinburg, 620990 Russia
e-mail: kozhevnikova@ihim.uran.ru

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Abstract—A convenient and effective one-pot three-component synthesis of the lead sulfide nanoparticles was developed on the basis of the exchange reaction between the lead acetate and sodium sulfide in water at the ambient conditions. A possibility was shown of the direct reaction between the lead Pb^{2+} and sulfide S^{2-} ions in an aqueous solution, resulting in a solid phase which contained PbS nanoparticles only, avoiding the hydrolysis stage.

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The synthesis approaches to the high-quality nanocrystals, in particular, the quantum dots with a high fluorescence yield and a narrow size distribution, can be reduced to two basic methods. The most common and studied of these is the high-temperature organometallic synthesis. This method was first published in 1993 [1, 2]. It consists in the obtaining inorganic nanoparticles in organic solvents. An alternative to the organometallic synthesis is the one-pot synthesis. At present it is widely used in organic synthesis, but is becoming more common also for obtaining inorganic compounds in the nanocrystalline state, for example, oxides [3] and the core-shell structures on the basis of pure metals [4] and metals chalcogenides [5], semiconductor nanocrystals and quantum dots [6–8]. Unlike the organometallic synthesis, the one-pot method makes it possible to synthesize the nanoparticles directly in the aqueous medium, i.e., to obtain water-soluble nanoparticles, that is a prerequisite for using these nanoparticles in the biological media. In addition, the one-pot synthesis is experimentally simpler method, and therefore it has a higher reproducibility and low cost.

A feature of the one-pot synthesis in aqueous solution is a possibility, besides the main reaction resulting in the inorganic nanoparticles, of occurrence the side reactions resulting in sparingly soluble in water oxygen-containing metal compounds. The probability of formation of these compounds is quite high, since the majority of metals ions in aqueous solution undergo hydrolysis. The hydrolysis processes complicates significantly the obtaining of pure nanoparticles containing no basic salts and hydroxides.

This paper describes the first use of the three-component one-pot synthesis of nanoparticles of the binary semiconductor compound, lead sulfide PbS, in an aqueous solution. Here, the characteristics of the crystal structure and phase composition of the obtained PbS nanoparticles are presented.

As both the $Pb(AcO)_2$ and Na_2S are readily soluble in water, at the first synthesis stage the solutions of strong electrolytes were obtained. As a result of the near-hydration phenomenon, i.e., due to the interaction of ions with the surrounding water molecules, all of the ions in the electrolyte solutions are hydrated. Thus, a solution of sodium sulfide is composed of the water molecules, the hydrated sodium and sulfide ions: H_2O, Na^{+}_{aq}, S^{2-}_{aq}. Another solution, a solution of lead acetate, contains the water molecules and the hydrated lead and acetate ions: H_2O, Pb^{2+}_{aq}, AcO^{-}_{aq}.

When mixing the two solutions, the main reaction occurs between the lead and sulfur ions to form the poorly soluble sulfide PbS_s [Eq. (1)].

$$Pb^{2+}_{aq} + S^{2-}_{aq} = PbS_s. \quad (1)$$

All the reactions discussed in this paper occur in the aqueous medium, so further such subscripts as aq (hydrated) and s (precipitate) will be used only for neutral molecules and precipitates, for example, $Pb(OH)_{2aq}$ or $Pb(OH)_{2s}$.

In the real experimental conditions, the formation of poorly soluble PbS_s compound by the reaction (1) is only one of the occurring chemical reactions. The reason for the other possible reactions is chemical interaction of water with the various compounds, i.e., the hydrolysis processes. Thus, hydrolysis of metal ions may lead to the formation of hydrates, hydroxo complexes, hydrolytic polymers [19] and compounds, which are sparingly soluble in water. Hydrolysis of weak acid anions often leads to the formation of the hydrated anions with higher charge, or the molecules of these acids. Taking into account that the hydrolysis of Na_2S proceeds only involving the anion, the chemical transformation involving the hydrated Pb^{2+}, AcO^- and S^{2-} ions in an aqueous solution, like any other chemical transformations, can be represented by a set of the reversible elementary reactions (2)–(20) [10].

$$Pb^{2+} + H_2O \rightleftarrows PbOH^+ + H^+, \tag{2}$$

$$Pb^{2+} + 2\,H_2O \rightleftarrows Pb(OH)_{2aq} + 2H^+, \tag{3}$$

$$Pb^{2+} + 3\,H_2O \rightleftarrows Pb(OH)_3^- + 3H^+, \tag{4}$$

$$3\,Pb^{2+} + 4\,H_2O \rightleftarrows Pb_3(OH)_4^{2+} + 4H^+, \tag{5}$$

$$4\,Pb^{2+} + 4\,H_2O \rightleftarrows Pb_4(OH)_4^{4+} + 4H^+, \tag{6}$$

$$6\,Pb^{2+} + 8\,H_2O \rightleftarrows Pb_6(OH)_8^{4+} + 8H^+, \tag{7}$$

$$2\,Pb^{2+} + H_2O \rightleftarrows Pb_2OH^{3+} + H^+, \tag{8}$$

$$Pb^{2+} + AcO^- \rightleftarrows PbAcO^+, \tag{9}$$

$$Pb^{2+} + 2\,AcO^- \rightleftarrows Pb(AcO)_{2aq}, \tag{10}$$

$$Pb^{2+} + 3\,AcO^- \rightleftarrows Pb(AcO)_3^-, \tag{11}$$

$$Pb^{2+} + 4\,AcO^- \rightleftarrows Pb(AcO)_3^{2-}, \tag{12}$$

$$AcO^- + H_2O \rightleftarrows AcOH_{aq} + H^+, \tag{13}$$

$$S^{2-} + H_2O \rightleftarrows HS^- + OH^-, \tag{14}$$

$$HS^- + H_2O \rightleftarrows H_2S_{aq} + OH^-, \tag{15}$$

$$Pb^{2+} + HS^- \rightleftarrows Pb(HS)_{2aq}, \tag{16}$$

$$PbOH^+ + AcO^- \rightleftarrows Pb(OH)AcO_s, \tag{17}$$

$$PbOH^+ + S^{2-} \rightleftarrows (PbOH)_2S_s, \tag{18}$$

$$PbOH^+ + H_2O \rightleftarrows Pb(OH)_{2s} + 2H^+, \tag{19}$$

$$Pb^{2+} + S^{2-} \rightleftarrows PbS_s. \tag{20}$$

The reaction affording the polynuclear lead hydroxo complexes (5)–(8) have been described in [11]. A reversibility sign $\rightleftarrows$ in the reactions (17)–(20) indicates that the poorly and sparingly soluble substances $Pb(OH)AcO_s$, $(PbOH)_2S_s$, $Pb(OH)_{2s}$, and PbS_s, remaining in a contact with the solution, do not leave the reaction sphere due to their non-zero solubility. To construct the total equation of the chemical reaction of the Pb^{2+}, AcO^- and S^{2-} ions in an aqueous solution is not reasonable, because the reactions (2)–(20) are reversible and are not mutually depending. Thus, in the reaction of $Pb(AcO)_2$ and Na_2S aqueous solutions, along with the expected product, the PbS nanoparticles, formation is possible of the hydrolysis products, as observed experimentally. It is difficult to predict theoretically which of these chemical reactions (2)–(20) will proceed and their deepness in this system. For most of the reactions (2)–(16) the direct and reverse reactions extent are comparable and depend on the pH value. The methods for describing these chemical transformations are described in detail in [10] and require large experimental work to determine the increment in the moles number of the product of the direct or reverse elementary reactions.

In this work, we describe quantitatively only the chemical transformation stages, for which the reverse elementary reaction can be neglected. These stages are usually qualified as irreversible, and in our case, these can include the reaction (17)–(20). At the synthesis of PbS nanoparticles in the three-component solution, we studied the composition, structure and microstructure of the precipitates resulting from the reactions (17)–(20). The liquid phase composition was not studied at this stage of the research.

The table presents the synthesis conditions and quantitative results of the X-ray diffraction analysis for the three most typical precipitates (Fig. 1), containing at least 85 wt % of the nanocrystalline PbS. The minimal initial concentration of the aqueous solutions of the starting materials, in which it was possible to synthesize PbS with an average particle size of not more than 20 nm and the impurity phases content not more than 15 wt %, is 0.005 M. At the lower concentrations, the content of the hydrolysis products, i.e., oxygenated phases, in the precipitates increases dramatically. At an initial concentration of $Pb(AcO)_2$ and Na_2S solutions of 0.0025 M the PbS phase in the precipitate was not found. This experimental fact is explained by the influence of dilution, at which there is a simultaneous decrease in the concentration of all the particles in a solution, except for the water molecules. In accordance with the principle of Le Chatelier, such exposure leads to a shift in equilibrium toward the reaction proceeding with the increasing particles number. The hydrolysis reaction is known to

Synthesis conditions, parameters of PbS nanoparticles and qualitative and quantitative composition of the precipitates by the X-ray diffraction

Comp. no.	Initial concentrations of the components in solution, M		Average particle size <*D*> PbS, nm	Period of a crystal lattice *a*, nm	Phase content, wt %			
	$Pb(AcO)_2$	Na_2S			PbS	$Pb(OH)_2$	NaHS	$PbSO_3$
I	0.005	0.005	20±3	0.5938±0.0003	99±1	–	–	–
II	0.025	0.025	15±3	0.5940±0.0003	90±1	–	–	10±1
III	0.25	0.25	16±3	0.5934±0.0003	90±1	4±1	2±1	4±1

occur always with an increase in the number of all the particles other than water, so the solution with initial concentration of less than 0.005 M the equilibrium shifts towards the hydrolysis reaction; and the hydrolysis extent increases both in the initial solutions and after mixing. In addition, when the solutions of concentration < 0.005 M are mixed, the reactions (13)–(15) and (17)–(19) equilibria are shifted to the right also because of the mutual facilitating the hydrolysis. According to the diffraction phase analysis, in this case the sparingly soluble precipitates are the lead basic salts and hydroxides. This is in accordance with the modern notions about the hydrolysis process.

In the initial concentration range of $0.005\ M \leq [Pb(AcO)_2] = [Na_2S] < 0.025\ M$ the powder precipitates of PbS nanoparticles, containing no other solid phases (see the table), were obtained. Probably, in this concentration range at the mixing $Pb(AcO)_2$ and Na_2S solutions the equilibrium of the reactions (13)–(15) and (17)–(19) is shifted not to the right, as might be expected, but rather to the left due to the binding the lead ions into the practically water-insoluble PbS_s in the reaction (20).

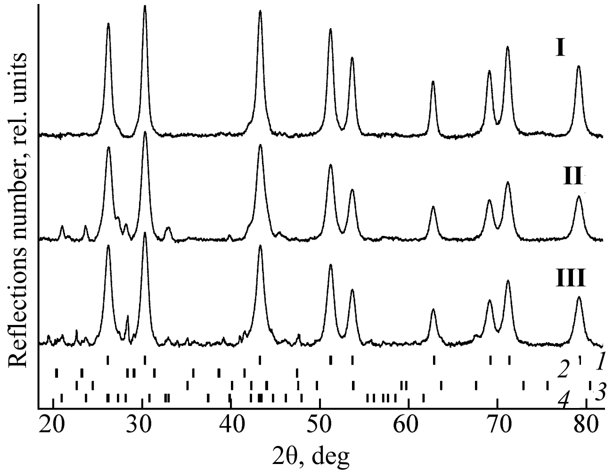

Fig. 1. X-Ray patterns of the most characteristic precipitates (see the table), which include nanocrystalline PbS in an amount not less than 85 wt%. The vertical solid lines show the reflections positions for those present in the precipitates of the crystalline phases: (*1*) PbS, (*2*) $Pb(OH)_2$, (*3*) NaHS, and (*4*) $PbSO_3$. The intensity is represented on a logarithmic scale.

At the initial concentrations $[Pb(AcO)_2] = [Na_2S] = 0.025–0.25\ M$ the main precipitate phase formed is the nanocrystalline PbS. The diffraction phase analysis (see the table) revealed the presence of oxygen-containing phases. The formation of small amount of lead hydroxide $Pb(OH)_{2s}$ (up to 5 wt % at $[Pb(AcO)_2] = [Na_2S] = 0.25\ M$), the product of the complete hydrolysis of Pb^{2+} ions, can be explained by the high ionic product at these initial concentrations of the salt and increase the pH value for the initial solution of Na_2S salt because of the reaction (14) occurrence. An evidence of the reaction (14) occurrence is the presence of sodium hydrosulfide $NaHS_s$ in the precipitate. The soluble phase of $NaHS_s$ was probably formed at the stage of drying due to experimental error during the precipitate washing. In addition, the solubility product of $Pb(OH)_{2s}$ is low ($K_{sp} = 1.1\times10^{-20}$ [12]), which exceeds only the solubility product for PbS_s (K_{sp} 2.5×10^{-27} [12]). The remaining poorly soluble solid phases that can form in this solution (17)–(18) are more soluble and not formed under the discussed the of synthesis conditions.

In the precipitates obtained at the initial concentrations of the components of 0.025–0.25 M presents the poorly soluble solid phase of lead sulfite $PbSO_{3s}$ (see the table). Its formation is due to the oxidation of PbS_s nanoparticles surface directly in the reaction mixture. Similar nanoparticle oxidation processes in aqueous solutions are observed in other metal chalcogenides [13]. Thus, it is necessary to add an irreversible redox reaction (21), where an oxidizing agent is obviously the dissolved oxygen, to the set of the reversible elementary reactions (2)–(20), which

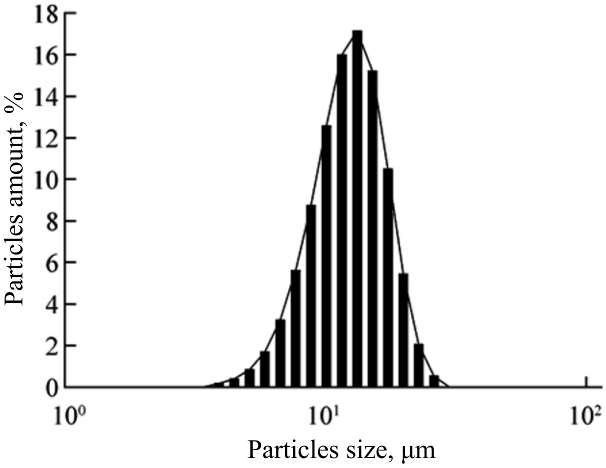

Fig. 2. Size distribution of the particles in the lead sulfide powder, obtained from aqueous solution with the initial concentrations of the salts $[Pb(AcO)_2] = [Na_2S] = 0.25$ M (sample **III** in the table).

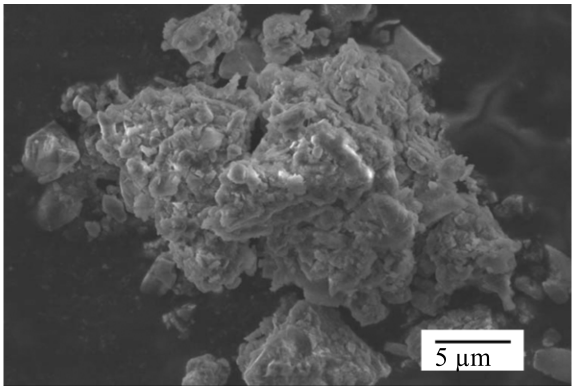

Fig. 3. Micrograph of the nanocrystalled lead sulfide, obtained from aqueous solution with the initial concentrations of the salts $[Pb(AcO)_2] = [Na_2S] = 0.005$ M (sample **I** in the table).

describe the chemical transformation to the original three-component solution.

$$2\,PbS_s + 3O_2 = 2\,PbSO_{3s}. \qquad (21)$$

The X-ray patterns of the precipitates containing PbS nanopowders are shown in Fig. 1. Average grain size <*D*> in powders PbS_1, PbS_2 and PbS_3, found by the Debye–Scherrer formula [14], is 20±3, 15±3 and 16±3 nm, respectively (see the table). The size and deformative contributions to the broadening of diffraction reflections were separated by the Williamson–Hall method [15, 16]. As a result, the microstresses in the PbS grains were found to be virtually absent. A structure *B*1 (of NaCl type, space group $Fm\overline{3}m$) with isotropic mean-square displacements of the lead and sulfur atoms was considered as a PbS structure model [17]. The structure refinement revealed that all PbS nanocrystalline particles obtained in this work have a cubic phase with *B*1 structure.

To determine the size distribution of PbS agglomerates we performed the dimensional-dispersion analysis. The sample **III** the agglomerate size ranges from 7 to 20 μm, and the average size of PbS agglomerates is 12 μm (Fig. 2). The scanning electron microscopy data (Fig. 3) also confirm these results. The 5000 times zoom of the PbS powder (Fig. 3) allows to see the large individual agglomerates of irregular shape. In conjunction with the X-ray analysis, the large sizes of the agglomerates indicate a strong particles agglomeration, up to 10^9 of PbS particles in an agglomerate. Such strong agglomeration suggests that surface of the synthesized PbS particles is hydrophobic.

Thus, this study demonstrated the feasibility of the obtaining nanocrystalline lead sulfide in the lead acetate–sodium sulfide–water ternary system under the ambient conditions. The three-component one-pot synthesis method is based on the exchange reaction between lead acetate and sodium sulfide in water. The main drawback of this method is that the direct interaction of lead Pb^{2+} and sulfide S^{2-} ions in an aqueous solution is always accompanied by hydrolysis processes, which leads to the formation of poorly soluble impurity phases. In addition, as was first observed in this study, the oxidation of PbS nanoparticles to lead sulfite begins at the ambient temperature, either directly in solution or on the stage of the precipitate drying. However, in the course of the experiment it was shown that the direct interaction of lead Pb^{2+} and sulfide S^{2-} ions in aqueous solution, leading to the formation of only PbS nanoparticles in the precipitate with the hydrolysis and oxidation stages escape, is possible.

EXPERIMENTAL

For the one-pot three components synthesis of PbS nanoparticles in an aqueous solution were used: lead acetate $Pb(AcO)_2$, sodium sulfide Na_2S and water. The synthesis was carried out under the ambient conditions (298 K, 1 atm). The initial concentrations (in the scale of the numerical density of the components moles) of aqueous solutions of $Pb(AcO)_2$ and Na_2S salts were varied in the range of 0.0025–0.25 M. For the each reaction the solutions of $Pb(AcO)_2$ and Na_2S were taken in stoichiometric amounts and mixed with vigorous stirring. The pH value was controlled with a pH/Ion Meter SyberScan 2100 (Eutech Instruments) ionomer with CyberComm Pro 2.4 DAS Sortware. The solutions pH in the synthesis of PbS nanoparticles was in the range of 4.75–6.25. The obtained precipitates were washed with distilled water, filtered off and air dried at room temperature.

All the samples of the solid phase were investigated by the X-ray diffraction method using a Philips X'Pert autodiffractometer at Cu$K_{\alpha1,2}$-irradiation. The X-ray measurements were carried out by the Bragg–Brentano method at Cu$K_{\alpha1,2}$-irradiation in the 2θ angle range of 17°–82° with a step Δ(2θ) 0.016 deg/sec. A Philips X'Pert diffractometer was equipped with a high-speed sectoral position-sensitive X'Celerator detector [18, 19], which reduces about 100-fold the duration of the X-ray shooting of nanopowders (from 200–300 h with conventional detector to 2–3 h with the X'Celerator detector) without losing the resolution quality for a large exposure time (300 s at each point). When choosing the optimal time of exposure, we accounted for such factors as sufficient intensity for the phase analysis, high signal–noise ratio, and a relatively short duration of the shooting. Qualitative and quantitative phase composition of the synthesized solids was determined using the Match! software package. Determination of the lattice parameters and the structure refinement of PbS nanoparticles was performed using the X'Pert Plus Ver. 1.0 program package.

The average size of the coherent scattering in the nanostructured precipitates was determined by the X-ray diffraction by the reflections broadening [20, 21]. The particles size distribution in the precipitates was determined using a HORIBA Partica LA-950V2 analyzer.

The particle size was evaluated and the microstructure of the obtained precipitates was observed using the scanning electron microscopy on a Jeol-JSM LA 6390 microscope equipped with a JED-2300 energy dispersive analyzer.

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REFERENCES

1. Murray, C.B., Nirmal, M., Norris, D.J., and Bawendi, M.G., *Zeitschrift fur Physik D: Atoms, Molecules and Clusters*, 1993, vol. 26, no. 1, p. 231.
2. Murray, C.B., Norris, D.J., and Bawendi, M.G., *J. Am. Chem. Soc*., 1993, vol. 115, no. 19, p. 8706.
3. Zeng, Y., Hao, R., Xing, B., Hou, Y., and Xu, Z., *Chem. Commun*., 2010, vol. 46, no. 22, p. 3920.
4. Hongchen Dong, H., Zhu, M., Yoon, J.A., Gao, H., Jin, R., and Matyjaszewski, K., *J. Am. Chem. Soc*., 2008, vol. 130, no. 39, p. 12852.
5. Gu, Z., Zou, L., Fang, Z., Zhu, W., and Zhong, X., *Nanotechnology*, 2008, vol. 19, no. 13, p. 135604.
6. Yong, K.-T., Sahoo, Y., Swihart, M.T., and Prasad, P.N., *J. Phys. Chem*., 2007, vol. 111, no. 6, p. 2447.
7. Kairdolf, B.A., Smith, A.M., and Nie, S., *J. Am. Chem. Soc*., 2008, vol. 130, no. 39, p. 12866.
8. Tang, A., Qu, S., Li, K., Hou, Y., Teng, F., Cao, J., Wang, Y., and Wang, Z., *Nanotechnology,* 2010, vol. 21, no. 28, p. 285602.
9. Nazarenko, V.A., Antonovich, V.P., and Nevskaya, E.M., *Gidroliz ionov metallov v razbavlennykh rastvorakh* (Hydrolysis of Metal Ions in Diluted Solutions), Moscow: Aomizdat, 1979.
10. Bulatov, N.K. and Lundin, A.B., *Termodinamika neobratimykh fiziko-khimicheskikh protsessov* (Thermodynamics of Irreversible Physical and Chemical Processes), Moscow: Khimiya, 1984.
11. Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjoberg, S., and Wanner, H., *Pure Appl. Chem*., 2009, vol. 81, no. 12, p. 2425.
12. Lur'ye, Yu.Yu., *Spravochnik po analiticheskoi khimii* (Handbook of Analytical Chemistry), Moscow: Khimiya, 1971.
13. Dabbousi, B.O., Rodriguez-Viejo, J., Mikulec, F.V., Heine, J.R., Mattoussi, H., Ober, R., Jensen, K.F., and Bawendi, M.G., *J. Phys. Chem. B*, 1997, vol. 101, no. 46, p. 9463.
14. Scherrer, P., *Nachr. Ges. Wiss. Gottingen, Math.-Ohys. Kl*., 1918, vol. 2, p. 98.
15. Hall, W.H. and Williamson, G.K., *Proc. Phys. Soc. London., B*, vol. 64, no. 383, p. 937.
16. Williamson, G.K. and Hall, W.H., *Act. Metal*., vol. 1, no. 1, p. 22.
17. Noda, Y., Ohba, S., Sato, S., and Saito, Y., *Acta Crystallogr., B*, 1983, vol. 39, no. 3, p. 312.
18. Morton, R.W., Simon, D.E., Gislason, J.J., and Taylor, S., *Advances in X-ray Analysis*, 2003, vol. 46, no. 1, p. 80.
19. Sadovnikov, S.I. and Rempel', A.A., *Fizika Tverdogo Tela*, 2009, vol. 51, no. 11, p. 2237.
20. Sadovnikov, S.I., Gusev, A.I., and Rempel', A.A., *Pis'ma v ZhETF,* 2009, vol. 89, no. 5, p. 279.
21. Rempel', A.A., *Usp. Khim.,* 2007, vol. 76, no. 5, p. 474.