Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Radiolytic synthesis of prismatical $PbSO_4$ microcrystals

Jing Zhou, Hongkai Zhao, Jianfeng Shi, Qingde Chen *, Xinghai Shen **

Beijing National Laboratory for Molecular Sciences (BNLMS), Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

ARTICLE INFO

Article history:
Received 9 April 2013
Accepted 29 July 2013
Available online 9 August 2013

Keywords:
Lead sulfate
γ-Irradiation
Controlled release
EDTA
Microcrystal

ABSTRACT

The prismatical $PbSO_4$ microcrystals were successfully synthesized by precipitating Pb^{2+} ions with SO_4^{2-} ions, which were generated from the reduction of $K_2S_2O_8$ in the presence of EDTA under N_2 atmosphere by γ-irradiation. It was found that EDTA and the controlled release of SO_4^{2-} play important roles in the formation of the microcrystals.

1. Introduction

Lead sulfate ($PbSO_4$), commonly known as anglesite, has been widely used as scintillator material, electrode material for storage batteries, white dye, quickly dried-paint and so on (Deng et al., 2009; Shao et al., 2005; Xiang et al., 2005). Thus, much effort has been paid to the preparation of $PbSO_4$. In general, $PbSO_4$ is synthesized by adding SO_4^{2-} ions directly into the solution containing Pb^{2+} or complexes of Pb^{2+}. Besides, Pb, PbO and PbO_2 can also be used as the lead sources (Xiang et al., 2005), and sodium dodecyl sulfate can be used as the source of SO_4^{2-} (Salavati-Niasari et al., 2012). Up to now, many $PbSO_4$ particles with different morphologies have been synthesized, for example, rod-like nano- and micro-crystals (Shao et al., 2005; Xiang et al., 2005), highly ordered lamellar mesostructure (Deng et al., 2009), plate-like nanocrystals (Zhou et al., 2002), and nanocubes (Katayama et al., 2004; Salavati-Niasari et al., 2012). However, except for nanocubes, the syntheses of $PbSO_4$ particles with other shapes need the help of the soft templates formed by surfactants and polyelectrolytes, *i.e.*, microemulsion (Xiang et al., 2005; Zhou et al., 2002), micelles (Shao et al., 2005), and layered mesophase (Deng et al., 2009). Therefore, it is worthwhile exploring the template-free preparation of $PbSO_4$ particles.

Ionizing radiation (such as γ-irradiation, electron beam irradiation and so on) has been widely used in preparing metal, core–shell metal or alloy, and metal chalcogenide particles (Belloni, 2006; Chen et al., 2010). However, to the best of our knowledge, there is no report on the radiolytic syntheses of $PbSO_4$ particles. Recently, we obtained $BaSO_4$ microspheres, mainly consisting of quasi-spherical nanoparticles, by precipitating Ba^{2+} ions with SO_4^{2-} ions, which were generated *via* the radiolytic reduction of $S_2O_8^{2-}$ (Chen et al., 2008; Chen and Shen, 2010). Nevertheless, as to $PbSO_4$, its solubility ($pK_{sp}=7.60$) is much larger than that of $BaSO_4$ ($pK_{sp}=9.97$) (Dean, 1999). Moreover, the cumulative formation constant for Pb^{2+} with EDTA ($\log\beta=18.3$) is considerably larger than that for Ba^{2+} ($\log\beta=7.78$) (Dean, 1999). Thus, under the precious condition for the radiolytic syntheses of $BaSO_4$, no $PbSO_4$ particles were obtained. There still remains a challenge. Herein, we report the radiolytic syntheses of prismatical $PbSO_4$ microcrystals without the assistant of template, and the effects of EDTA and the controlled release of SO_4^{2-} on their morphology.

2. Experimental

An aqueous solution containing 4.0 mmol/L $Pb(NO_3)_2$, 4.0 mmol/L $K_2S_2O_8$ and 4.0 mmol/L disodium ethylenediaminetetraacetate (EDTA) was prepared. The pH value of the solution was adjusted to 1.0 by 4.0 mol/L HNO_3 solution. After bubbling with high-purity N_2 under anaerobic conditions for 20 min, the solution was irradiated in the field of a ^{60}Co γ-ray source. The dose rate was 60 Gy/min and the absorbed dose was 6 kGy unless otherwise stated.

After irradiation, white precipitates were obtained and washed with water, and then dispersed in water. The obtained dispersion was dropped onto a Formvar-covered copper grid placed on a filter paper. After the solvent was evaporated at room temperature, the scanning electron microscopy (SEM) images were obtained *via* a FEI NanoSEM 430 scanning electron microscope operated at 3 or 15 kV. The range of particle sizes was determined by measuring the dimensions of more than 100 particles on the micrographs. In addition, after the dispersed

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.07.027

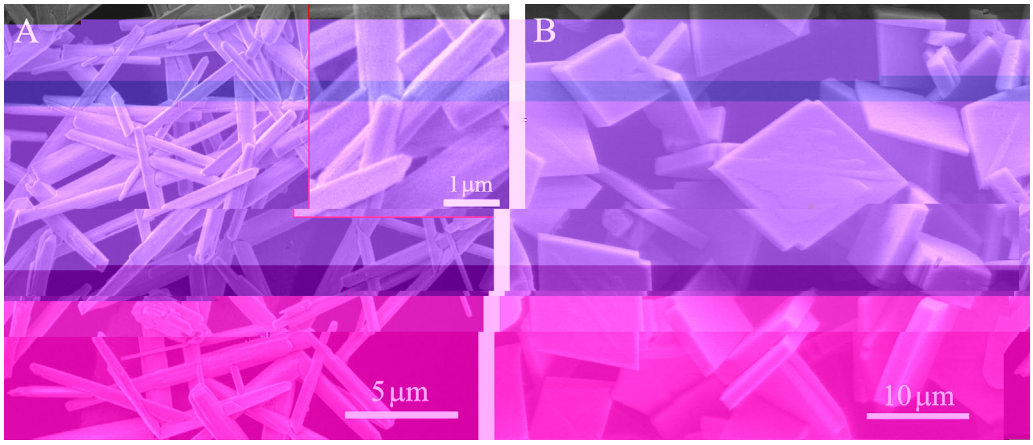

Fig. 1. SEM images of the samples synthesized in the presence (A) and absence (B) of EDTA by γ-irradiation. The inset in (A) shows the image of the sample at higher magnification.

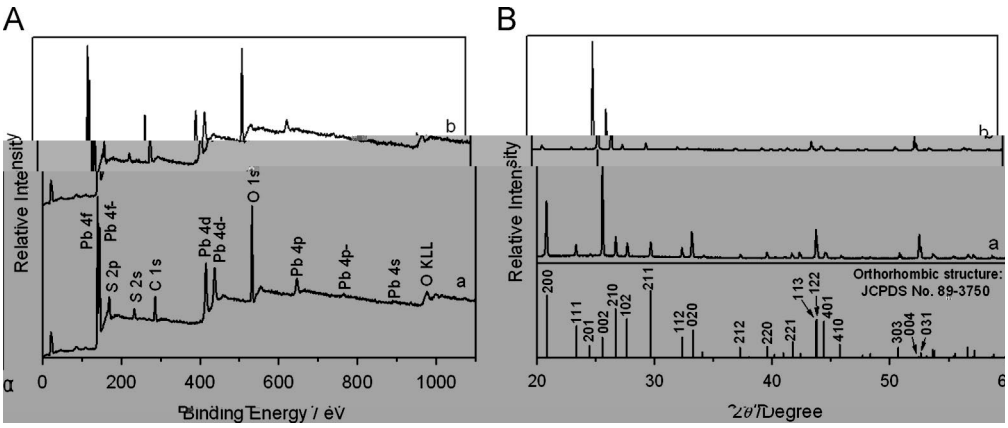

Fig. 2. X-ray photoelectron spectra (A) and XRD patterns (B) of the obtained samples synthesized in the presence (a) and absence (b) of EDTA by γ-irradiation.

sample was deposited on a piece of glass, the powder X-ray diffraction (XRD) pattern was recorded on a D/MAX-PC2500 diffractometer with Cu Kα radiation ($\lambda = 0.154056$ nm) and the X-ray photoelectron spectrum (XPS) was collected on a Kratos Axis Ultra spectrometer with monochromatized Al Kα radiation.

3. Results and discussion

Fig. 1A presents the SEM images of the obtained sample. It can be seen that the product is composed of rod-like microcrystals, with an average length of *ca.* 5 μm. From the SEM image at higher magnification (inset, Fig. 1A), most of the end of the microcrystals is triangle, with an average side length of *ca.* 500 nm. In other words, the microcrystals are prismatical, whose average aspect ratio is *ca.* 10. The related XPS analysis (curve a, Fig. 2A) shows that the binding energies of Pb 4f, S 2p and O 1s are 139.15, 168.15 and 531.15 eV, respectively, close to the values of Pb^{2+} and SO_4^{2-} reported in the literature (Moulder et al., 1992). Furthermore, the analysis result also exhibits the presence of Pb, S and O in the ratio of 1.0:1.0:4.1, close to the stoichiometry of $PbSO_4$ within experimental error. Thus, it can be deduced that $PbSO_4$ was generated. The corresponding XRD pattern (curve a, Fig. 2B), which is consistent with the orthorhombic $PbSO_4$ structure, further demonstrates the generation of $PbSO_4$.

In our experiment, when the solution was irradiated by γ-rays, the water molecules absorbed the irradiation energy and generated many reactive species, such as hydrated electrons (e_{aq}^-), H and •OH (Eq. (1)) (Buxton et al., 1988):

$$H_2O \xrightarrow{\text{irradiated}} e_{aq}^-,\ H,\ \bullet OH,\ \cdots \quad (1)$$

Then, •OH was eliminated by EDTA (Buxton et al., 1988; Sahul, 1987), with a rate constant of 4.0×10^8 L mol^{-1} s^{-1}, and the reducing

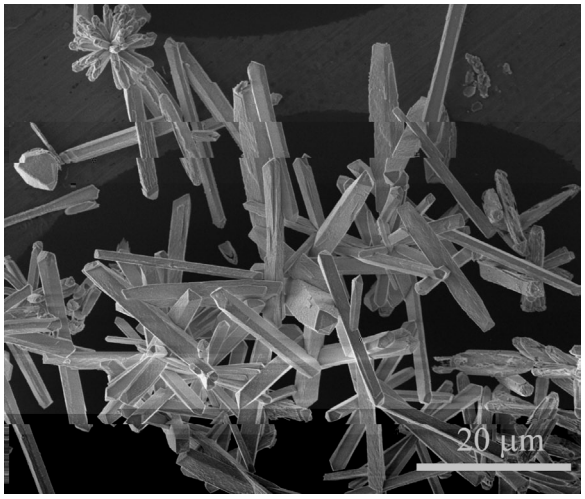

Fig. 3. SEM image of the sample synthesized by the addition of 4 mmol/L $Pb(NO_3)_2$ into the irradiated mixed solution (pH = 1.0) of 4 mmol/L EDTA and 4 mmol/L $K_2S_2O_8$.

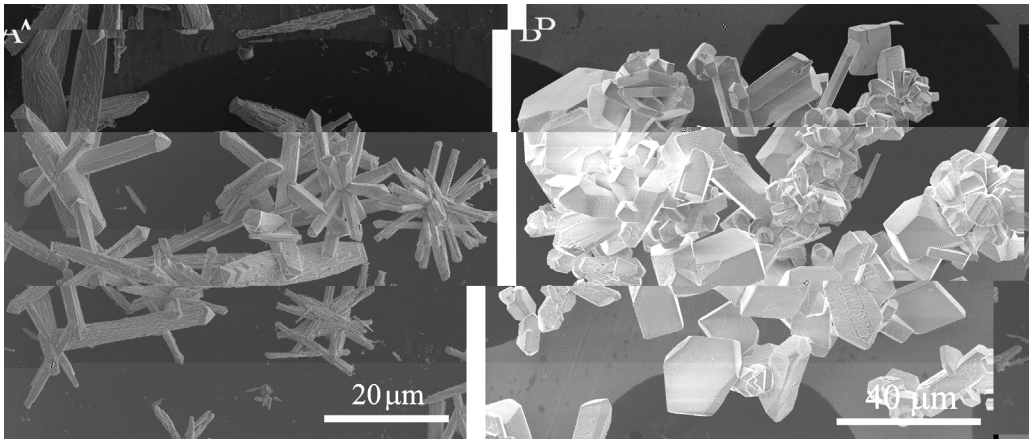

Fig. 4. SEM images of the samples synthesized at the different dose rate: (A) 110 Gy/min, and (B) 300 Gy/min.

species, especially e^-_{aq}, reduced $S_2O_8^{2-}$ ions to SO_4^{2-} ions (Eq. (2)), with a rate constant of 1.2×10^{10} L mol^{-1} s^{-1} (Buxton et al., 1988).

$$S_2O_8^{2-} + e^-_{aq} \rightarrow SO_4^{2-} + SO_4^{-}\bullet \quad (2)$$

Thus, the controlled release of SO_4^{2-} and the following generation of $PbSO_4$ could be realized.

To explore the effect of the controlled release of SO_4^{2-} on the formation of $PbSO_4$ microcrystals, a control experiment was performed, in which the mixed solution (pH = 1.0) of 4 mmol/L $K_2S_2O_8$ and 4 mmol/L EDTA was irradiated under N_2 atmosphere. Then, 4 mmol/L $Pb(NO_3)_2$ solution was added into the solution and mixed rapidly. The mixture was left to stand under static conditions away from light at room temperature for 100 min to obtain the sample for SEM characterization. The SEM image (Fig. 3) shows that the obtained product is also composed of prismatical microcrystals. However, the distributions of their side length and aspect ratio become large obviously. Thus, it can be concluded that the controlled release of SO_4^{2-} is important to the formation of $PbSO_4$ microcrystals.

Besides, dose rate was used to adjust the controlled release of SO_4^{2-}. Generally, the higher dose rate lead to the higher reduction rate of precursors, much more crystal nucleus and the smaller particle size. However, in our experiment, when the dose rate increased from 60 Gy/min to 110 Gy/min, the obtained $PbSO_4$ particles are also prismatical microcrystals, but with a larger distribution of their side length and aspect ratio (Fig. 4A). Besides, the middle of some microcrystals swells slightly (Fig. 4A). When the dose rate increased to 300 Gy/min, some prismatical microcrystals with a low aspect ratio, as well as some plate-like and irregular microcrystals were generated (Fig. 4B). The side length of the first two kinds of microcrystals is evidently larger than that of the prismatical microcrystals formed at the dose rate of 60 Gy/min (Figs. 1A and 4B). This is different from the normal phenomena, suggesting that there are other factors in controlling the formation of $PbSO_4$ prismatical microcrystals besides the controlled release of SO_4^{2-}.

In the morphology and size control of $BaSO_4$, amino-carboxylate additives were found effective (Chen et al., 2008; Uchida et al., 2000). In this experiment, EDTA, one of the most common amino-carboxylate additives, was used. To investigate its effect, we carried out another control experiment, in which EDTA was not added. The obtained product is composed of plate-like microcrystals, with a height of 0.8–4 μm and a wide-distributed side length (Fig. 1B). The results of XPS and XRD analyses (curves b, Fig. 2) validate that the product is still $PbSO_4$. Moreover, the microcrystals belong to orthorhombic system determined by XRD analysis (curve b, Fig. 2B). In addition, when an aqueous solution containing 4.0 mmol/L $Pb(NO_3)_2$, 4.0 mmol/L $K_2S_2O_8$ and 8.0 mmol/L EDTA was irradiated, no $PbSO_4$ precipitation appeared. When the pH value was adjusted to 1.0, to weaken the coordination ability of EDTA, there was still no any sedimentation. This situation did not change until the concentration of EDTA was reduced to 4.0 mmol/L at the pH value of 1.0. Therefore, it is reasonable to deduce that EDTA plays an important role in the formation of prismatical $PbSO_4$ microcrystals.

In the irradiation course, it may be the controlled release of SO_4^{2-} and the controlled release of Pb^{2+} through the dissociation of Pb-EDTA complex that retard the generation of $PbSO_4$. Furthermore, it may be the adsorption of EDTA on some special crystal faces of $PbSO_4$ nuclei that lead to the growth of $PbSO_4$ nuclei along some particular directions, resulting in the formation of prismatical morphology. However, this selective adsorption of EDTA may be weaker. With the increase of dose rate, the generation of $PbSO_4$ becomes quicker, and the action of EDTA becomes weaker gradually. Hence, it is not difficult to understand the generation of the prismatical microcrystals with a low aspect ratio, as well as the plate-like and irregular microcrystals at the dose rate of 300 Gy/min. Besides, the higher solubility is propitious to the ripening of $PbSO_4$ within a short time, resulting in the formation of microcrystals. With respect to $BaSO_4$, the materials with very low equilibrium solubility over a wide range of pH values, the molecular redissolution–crystallization events are suppressed to a great extent (Meldrum and Colfen, 2008), so the ripening need much longer time (Chen and Shen, 2010) and nanoparticles could be reserved.

4. Conclusions

The prismatical $PbSO_4$ microcrystals were successfully synthesized by precipitating Pb^{2+} ions with SO_4^{2-} ions, which were generated from the reduction of $K_2S_2O_8$ in the presence of EDTA under N_2 atmosphere by γ-irradiation. It was found that EDTA and the controlled release of SO_4^{2-} play important roles in the formation of the microcrystals. It is believed that the result reported herein will not only help understanding the effect of irradiation on the formation of inorganic particles, but also make the syntheses of micro- and nanocrystals more abundant.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grants nos. 91226112 and 20871009), the Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant no. 20110001120121) and the Coordinated Research Projects of International Atomic Energy Agency (Research Contract no. 15107).

Sincere thanks are due to Ms. Huizhen Zhang (PKU) for the help with SEM experiments. We also thank Dr. Jinglin Xie (PKU) for the help with XPS experiments and thank Mr. Deliang Sun (PKU) for the assistance in the γ-irradiation experiments.

References

Belloni, J., 2006. Nucleation, growth and properties of nanoclusters studied by radiation chemistry—application to catalysis. Catalysis Today 113, 141–156.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (.OH/.O^-) in aqueous-solution. Journal of Physical and Chemical Reference Data 17, 513–886.

Chen, Q.D., Bao, H. ., Shen, X.H., 2008. Radiolytic synthesis of $BaSO_4$ microspheres. Radiation Physics and Chemistry 77, 974–977.

Chen, Q.D., Shen, X.H., 2010. Formation of mesoporous $BaSO_4$ microspheres with a larger pore size via Ostwald ripening at room temperature. Crystal Growth and Design 10, 3838–3842.

Chen, Q.D., Shen, X.H., Gao, H.C., 2010. Radiolytic syntheses of nanoparticles in supramolecular assemblies. Advances in Colloid and Interface Science 159, 32–44.

Dean, J.A., 1999. Lange's Handbook of Chemistry, 15th ed. McGraw-Hill Professional, New ork.

Deng, B., Wang, C.C., Li, Q.G., Xu, A.W., 2009. Highly ordered lamellar mesostructure of nanocrystalline $PbSO_4$ prepared by hydrothermal treatment. Journal of Physical Chemistry C 113, 18473–18479.

Katayama, A., Sakuma, T., Hirasawa, I., 2004. Influence of polyethylenimine on the precipitation process of lead sulfate crystals. Journal of Crystal Growth 260, 500–506.

Meldrum, F.C., Colfen, H., 2008. Controlling mineral morphologies and structures in biological and synthetic systems. Chemical Reviews 108, 4332–4432.

Moulder, J.F., Stickle, W.F., Sobol, P.E., Bomben, K.D., 1992. Handbook of X-ray Photoelectron Spectroscopy. Perkin Elmer Physical Electronics Division, Eden.

Sahul, K., 1987. Radiolytic reduction of ferricethylenediaminetetraacetate in aqueous solution. Radiation Physics and Chemistry 30, 51–53.

Salavati-Niasari, M., Ranjbar, M., Mohandes, F., 2012. Self-assembly of cubic-like nanostructures to form star-like lead sulfate microstructures. Micro and Nano Letters 7, 581–584.

Shao, H.F., Zhang, .B., Qian, X.F., in, J., Zhu, Z.K., 2005. Preparation of rod-shape $PbSO_4$ nanocrystal and its phase transition to PbS. Materials Letters 59, 3507–3513.

Uchida, M., Sue, A., oshioka, T., Okuwaki, A., 2000. Hydrothermal synthesis of needle-like barium sulfate using a barium(II)-EDTA chelate precursor and sulfate ions. Journal of Materials Science Letters 19, 1373–1374.

Xiang, J.H., u, S.H., Geng, X., Liu, B.H., Xu, ., 2005. Growth of $PbSO_4$ single-crystal nanorods and optical properties by a microemulsion approach. Crystal Growth and Design 5, 1157–1161.

Zhou, H.C., Xu, J., Li, .D., 2002. Preparation and self-assemble of plate-like nanocrystal of $PbSO_4$ via microemulsions approach. Chemical Journal of Chinese Universities 23, 1645–1647.