

Y. J. Yang · L. Y. He

## Dissolution of lead electrode and preparation of rod-shaped PbS crystals in a novel galvanic cell

Received: 17 December 2004 / Revised: 7 April 2005 / Accepted: 9 May 2005 / Published online: 12 July 2005  
© Springer-Verlag 2005

**Abstract** A simple galvanic cell was developed to produce rod-shaped PbS crystals with lead and gold as negative and positive electrodes. The electrolyte solution contains sodium thiosulfate, sodium sulfate, and 1-thioglycerol (TG). It was found out that lead dissolved spontaneously and produced PbS crystals in the electrolyte solution immediately after assembling the cell. Further study shows that TG catalyzes the oxidation of lead into  $Pb^{2+}$  and the reduction of thiosulfate into  $S^{2-}$ . The produced rod-shaped PbS crystals are 140~350 nm in diameter and 1~3  $\mu\text{m}$  in length after 4 h of reaction.

**Keywords** Electrochemistry · Galvanic cell · Nanorods · Lead sulfide · Semiconductor

### Introduction

PbS is a typical narrow band gap semiconductor. It is one of the most attractive metal sulfide semiconductors for a wide variety of applications. Although numerous methods such as micelles [1, 2], polymers [3, 4], sol-gel technique [5], hydrothermal technique [6], electrochemistry [7], microwave irradiation, and ultrasonic irradiation [8] have been developed to fabricate PbS nanoparticles. So far, very few work has been done on the synthesis of rod-shaped PbS crystals except those which prepare rod-shaped PbS crystals in systems containing organic polyamines with N-chelation properties, such as triethylenetetramine [9] and ethylenedimine [10], respectively. However, a rather long reaction time was needed.

In this report, a novel galvanic cell was developed with lead as anode and gold as cathode in a one-com-

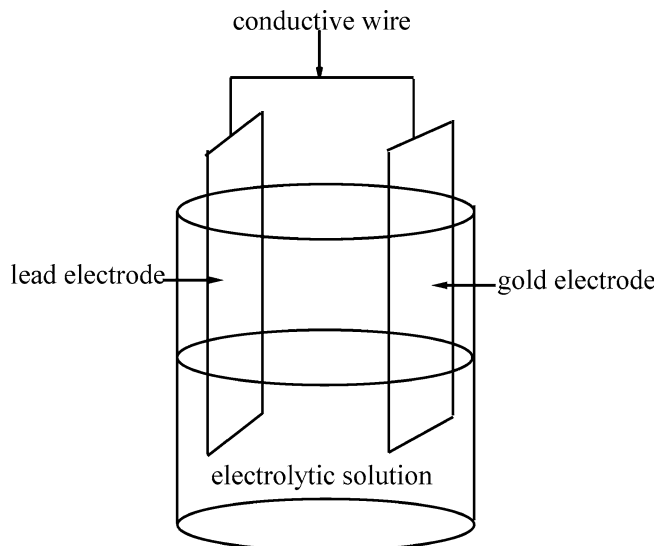
partment cell. The galvanic process has been applied earlier in the electroless deposition of  $\text{Cu}_2\text{Se}$  film on copper foil in sodium selenosulfate solution [11]. We discovered a similar reaction between lead foil and sodium thiosulfate solution. Rod-shaped PbS crystals were produced upon the immersion of both lead and gold electrodes in the electrolyte solution containing sodium thiosulfate, sodium sulfate, and 1-thioglycerol (TG).

### Materials and methods

A lead foil was degreased with acetone, cleaned with diluted nitric acid to remove the oxide layer, polished with soft tissue paper, rinsed with deionised water for several times, and dried with high purity nitrogen gas. A gold foil was polished to mirror-like surface with 0.3  $\mu\text{m}$  alumina slurry, electrochemically polished in 1 M sulfuric acid, and rinsed with distilled water for several times. The galvanic cell was set up as shown in Fig. 1. The lead foil was used as anode (negative electrode) and gold foil as cathode (positive electrode). The lead and gold foils were connected with a conductive wire and immersed in 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M TG aqueous solution under stirring.

Optical absorption spectrum was recorded using a Shimadzu UV-vis 265 spectrophotometer in the wavelength range of 250~500 nm at room temperature. X-ray powder diffraction (XRD) patterns were recorded using a SIEMENS X-ray diffractometer equipped with graphite monochromatized  $\text{Cu K}\alpha$  radiation source ( $\lambda=0.154178$  nm). A scanning rate of 0.02  $^\circ/\text{s}$  in  $2\theta$  ranges from  $10^\circ$  to  $90^\circ$  was used. Scanning electron microscope (SEM) images were carried out with a JEOL, JEM-6700 SEM. Transmission electron microscope (TEM) experiments were carried out employing Philips CM10 TEM, using an accelerating voltage of 100 kV. The samples used for TEM were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 15 min. Fourier transform infrared (FT-IR) spectra were recorded at room temperature on

Y. J. Yang (✉) · L. Y. He  
Zhongyuan Institute of Technology, Zhengzhou, Henan, 450007  
People's Republic of China  
E-mail: yangyujun@yahoo.com  
Tel.: +86-371-63671510



**Fig. 1** The setup of the galvanic cell. The composition of the electrolyte solution: 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M 1-thioglycerol (TG) aqueous solution

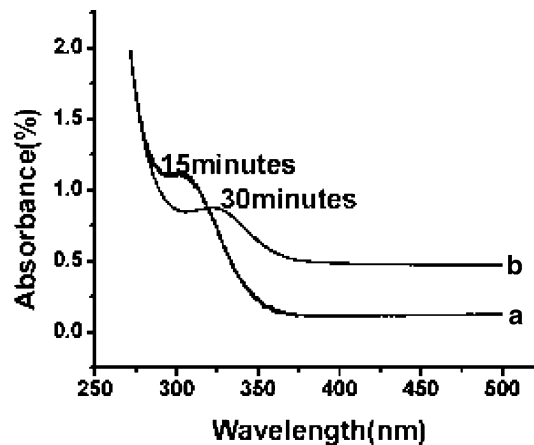
a BioRad FTS 575C FT-IR instrument. The KBr pellets were used as supporting materials for analysis. A powder specimen was used for recording spectra of rod-shaped PbS crystals.

## Results and discussion

The electrolyte solution changed from colorless to brown immediately at room temperature as both of gold ( $1 \times 4 \text{ cm}^2$ ) and lead ( $1 \times 4 \text{ cm}^2$ ) electrodes were immersed in 100 mL 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M TG aqueous solution. With the distance between lead and gold electrodes kept at 5 cm, 0.060 g PbS was finally obtained after 4 h of reaction under magnetic stirring with a PbS thin film deposited on the lead electrode surface. Investigation on the reaction mechanism reveals that TG catalyzes this galvanic reaction and no reaction will take place without the addition of TG.

At first, only very small PbS crystals were produced, which was confirmed by the UV-vis absorption spectrum of the produced PbS crystals after different reaction time. UV-vis has been used to determine both particle size and the degree of particles aggregation in the sample. As the particle size decreases, the  $\lambda_{\text{max}}$  shifts to shorter wavelengths due to the band gap increase of the smaller-sized particles [12, 13]. As shown in Fig. 2, well-defined absorption features were exhibited, which is due to UV absorption of the produced PbS crystals after 15 and 30 min of reaction.

The UV-vis absorption edge of these PbS crystals shows a very significant blue shift from the bulk PbS. As the reaction time was increased from 15 to 30 min, the absorption edge of PbS crystals shifted from 310 to 330 nm. This red shift is due to the growth of small PbS

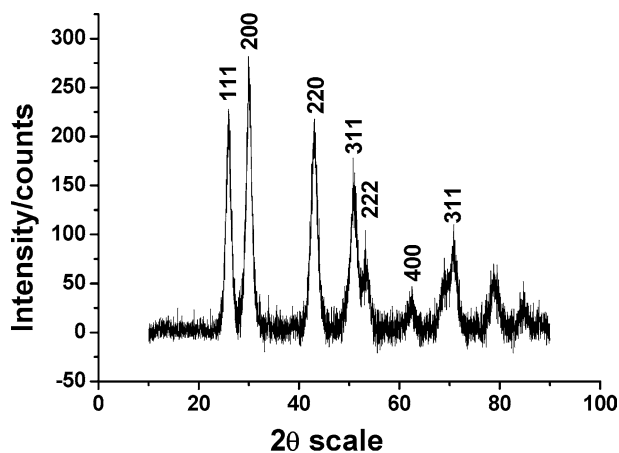


**Fig. 2** UV-vis absorption spectrum of the PbS crystals produced after 15 (a), 30 (b) minutes of reaction in 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M TG aqueous solution

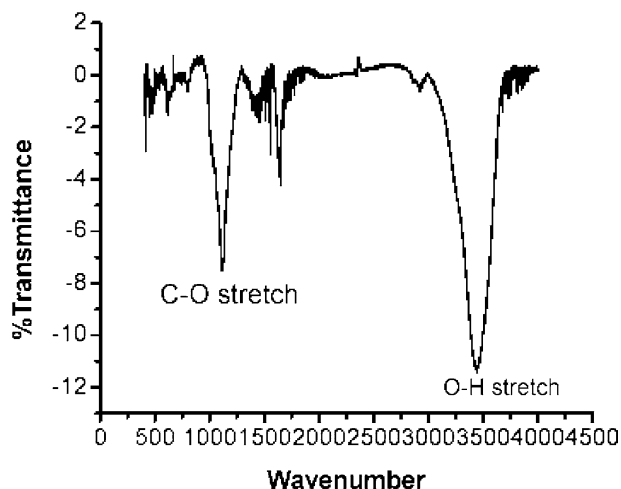
crystals into larger ones during the reaction. No absorption feature of PbS can be observed after 1 h of reaction. However, small crystals gradually grew into larger ones and eventually lead to the formation of large rod-shaped PbS crystals after 4 h of reaction.

X-ray diffraction (XRD) analysis was used to examine the crystal structure of the products. The XRD pattern of the as-synthesized PbS is shown in Fig. 3. All the diffraction peaks can be indexed to the cubic rock salt structure of PbS with lattice constant  $a = 5.9348 \text{ \AA}$ , which is in good agreement with the literature value (JCPDS No. 5-592). The strong and sharp peaks indicate that rod-shaped PbS crystals are highly crystalline.

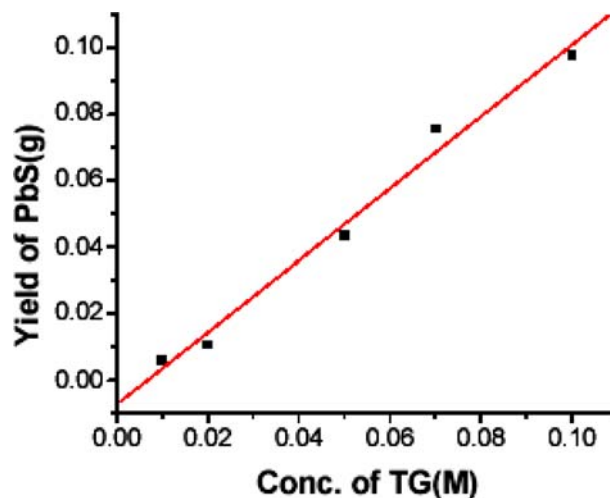
The FT-IR spectrum of the produced rod-shaped PbS crystals in Fig. 4 shows a strong and broad O-H stretching band at  $3,500 \text{ cm}^{-1}$  and a strong C-O stretching band at  $1,100 \text{ cm}^{-1}$ . The FT-IR spectra confirm (a) that the PbS crystals were capped with TG and



**Fig. 3** X-ray diffraction pattern of the rod-shaped PbS crystals synthesized in 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M TG under stirring for 4 h



**Fig. 4** Fourier transform infrared spectra of TG protected rod-shaped PbS crystals



**Fig. 5** The linear relationship between the concentration of TG and the yield of PbS after 4 h of reaction in 0.03 M sodium thiosulfate and 0.1 M sodium sulfate aqueous solution under stirring

**Table 1** The yield of PbS after 4 h of reaction in 100 mL 0.03 M sodium thiosulfate and 0.1 M sodium sulfate aqueous solution under stirring with different concentration of TG in the solution

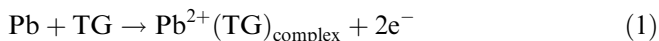
Concentration of TG (M)	0.01	0.02	0.05	0.07	0.10
Yield of PbS (g)	0.060	0.0108	0.0435	0.0757	0.098

(b) that the TG molecule is not leached out during several washings of the PbS crystals.

Not only acting as the capping agent of PbS crystals, TG also catalyzes the reaction between lead and thiosulfate (Table 1). Our experiment indicates that no reaction occurs without the addition of TG and TG cannot react with lead foil to produce PbS directly without the addition of sodium thiosulfate. Further study shows that the yield of PbS after 4 h of reaction increased almost linearly (Fig. 5) with the increasing concentration of TG. It can be concluded that the reaction rate is controlled by the concentration of TG. The higher the concentration of TG, the higher the reaction rate and more PbS were produced after the same reaction time.

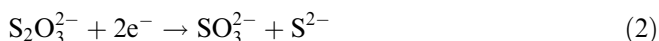
The proposed reaction mechanism consists of anodic lead oxidation coupled to cathodic generation of sulfide anions. The lead foil was used as a sacrificing anode and gold foil as a cathode. It is composed of two half-cell reactions:

On the lead anode, oxidation takes place.

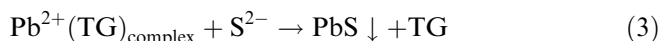


TG facilitates the lost of electrons and complexes with the produced lead cations.

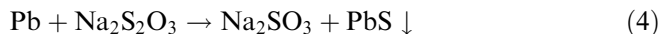
On the gold cathode, reduction takes place.



Finally,  $\text{S}^{2-}$  reacted with  $\text{Pb}^{2+}(\text{TG})$  to form PbS.



The total reaction can be written as:

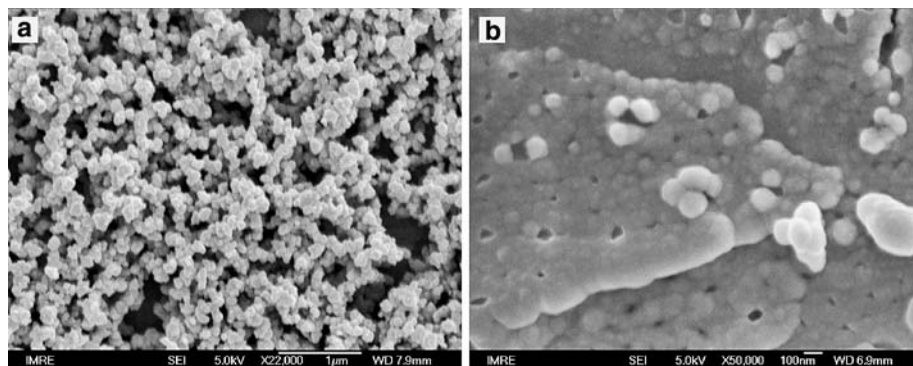


With the two half-cell reactions occurring in the same electrolyte solution, it is unavoidable to prevent the formation of PbS on the lead surface. PbS thin film was still observed although the stirring helps to remove the PbS from the lead electrode surface (Fig. 6). The PbS thin film on the lead is composed of cube-shaped PbS crystals in the size of 100~150 nm. The PbS crystals produced in the electrolyte solution have a different morphology than those formed on the electrode surface. Figure 7 shows the TEM image of rod-shaped PbS crystals as precipitated from the electrolyte solution when the galvanic reaction proceeded under stirring for 4 h with 0.01 M TG in the solution. Although some very large crystals did exist, most of the produced rod-shaped PbS crystals were around 200 nm in diameter and their lengths are in the range of 1~3  $\mu\text{m}$ .

## Conclusions

A novel galvanic reaction has been discovered. With lead as anode and gold as cathode, lead spontaneously dissolved and rod-like PbS crystals were produced in the sodium thiosulfate, sodium sulfate, and 1-thioglycerol aqueous solution. TG was discovered to catalyze this reaction. This galvanic reaction can be written as  $\text{Pb} + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{PbS} \downarrow$ . However, direct evidence is still needed to support the proposed mechanism. This galvanic synthetic technique may be a cheap, con-

**Fig. 6** Scanning electron microscope images of lead electrode surface after the reaction in 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M TG aqueous solution under stirring for 4 h, then **a** washed with deionised water; **b** washed with deionised water, and cleaned in ultrasonic bath for half an hour subsequently



**Fig. 7** Transmission electron microscope image of rod-shaped PbS crystals precipitate in the electrolyte solution after the reaction in 0.03 M sodium thiosulfate, 0.1 M sodium sulfate, and 0.01 M TG aqueous solution under stirring for 4 h

venient, and quick method to prepare PbS rod-shaped crystals. Our further study suggests the possibility of tuning the morphology of the produced PbS crystals by the addition of shape-driving agents and the adjusting of reaction time. The catalytic effect of TG on other metals in similar galvanic cell assemblies is currently under investigation in my lab.

## References

1. Eastoe J, Cox RA (1995) *Colloid Surf A* 101:63
2. Chakraborty I, Moulik SP (2004) *J Nanoparticle Res* 6:233
3. Zeng Z, Wang S, Yang S (1999) *Chem Mater* 11:3365
4. Kane RS, Cohen RE, Silbey R (1996) *Chem Mater* 8:1919
5. Martucci A, Innocenzi P, Fick J, Mackenzie JD (1999) *J Non-Cryst Solids* 244:55
6. Huang Q, Gao L (2004) *Chem Lett* 33:1338
7. Yang YJ, He LY, Zhang QF (2005) *Electrochem Comm* 7:361
8. Zhao Y, Liao XH, Hong JM, Zhu JJ (2004) *Mater Sci Phys* 87:149
9. Sugimoto T, Chen SH and Muramatsu A (1998) *Colloid Surf A* 135:207
10. Chen M, Xie Y, Yao Z, Qian Y and Zhou G (2002) *Mater Res Bull* 37:247
11. Schimmel MI, Bottechia OL and Wendt H (1998) *J Appl Electrochem* 28:299
12. Chestnoy N, Harris TD, Hull R and Brus LE (1986) *J Phys Chem* 90:3393
13. Wilcoxon JP, Newcomer PP, Samara GA (1997) *J Appl Phys* 81:7934