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General synthesis of metal sulfides nanocrystallines via a simple polyol route

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Abstract

In this report, a simple and easy polyol route for synthesizing many binary metal sulfides nanocrystallines is demonstrated. Powder X-ray electron diffraction and energy-dispersive X-ray spectrum are applied to investigate the crystallinity and composition of the nanoscale materials. The resulting particle size and morphology are examined by transmission electron microscopy, and the possible mechanism is also briefly discussed.

Keywords: Sulfides; Nanocrystallines; Polyol route

1. Introduction

Transition metal chalcogenides including sulfides, selenides and tellurides are often found in minerals and have attracted considerable attention in recent decades due to the interesting properties they possess [1]. They have a number of commercial applications in pigments, semiconductors, fluorescence devices and even superconductors [2,3]. With regard to all of the applications mentioned, highly crystalline particles with almost monodisperse size distribution and regular morphology are required. In fact, many different methods of preparation, liquid-based as well as gas phase-based, are aiming at the fulfillment of these requirements [4–8]. The polyol method applied herein provides a promising preparative approach to such sulfide particles.

The polyol method was initially described for the preparation of elemental metals and alloys [9–12], in which the reducing properties of a high-boiling alcohol (e.g. glycerol, glycol) towards a suitable metal precursor were utilized. Recently, a lot has been investigated on the preparation of metal oxide particles [13,14]. Generally, this solution reaction for the formation of binary chalcogenides is relatively slow; till now, the synthetic strategies based on the polyol route to binary chalcogenides are always conducted under microwave irradiation [15]. Our group also developed solvothermal route in polyol solvent to sulfides using autoclave as pressure equipment [16]. The direct polyol synthesis of binary metal sulfides under moderate conditions (without special high temperature and pressure or microwave irradiation, or sensitive reagents or expensive equipment) has seldom been reported except that of Feldmann [17].

In our present investigations, the polyol method was found to be suitable for the synthesis of a host of binary metal sulfides under moderate conditions.

2. Experimental

All reagents were of analytical purity and purchased from different chemical companies and used without further purification. Generally, appropriate amount of metal salts and thiourea were placed in a 100 mL round-bottomed flask. Then the flask was filled with 50 mL glycol solution. Stirred for a few seconds, the solution was heated and refluxed for 0.5–2 h. After the mixture had been cooled, the solid was filtered and washed several times with carbon bisulfide, absolute alcohol and distilled water. Then vacuum dried at 60°C for 3 h.

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X-ray powder diffraction (XRD) patterns were carried out on a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The samples were scanned at a scanning rate of 0.05°/s in the 2θ range of 15–70°. Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

3. Result and discussion

By refluxing different metal salts and thiourea (Tu) in glycol at appropriate conditions, various sulfides are obtained. The detail experimental results are shown in Table 1.

The phase purity of these products was determined by XRD procedure and energy-dispersive X-ray (EDX) spectrum. The microstructure was observed by TEM.

Table 1
X-ray powder diffraction data of the products from the reactions of thiourea and metal salts

Reactants	Reactive time (h)	Products	Morphology	JCPDS reference
$NiCl_2 \cdot 6H_2O + Tu$	1.5	NiS	Nanoparticles	75-0613
$CuCl + Tu$	1	$Cu_{1.8}S$	Nanoparticles	23-0962
$CuCl_2 \cdot 2H_2O + Tu$	1	$CuS + Cu_{1.8}S$[a]	Nanoparticles	/
$CuSO_4 \cdot 5H_2O + Tu$	1	$Cu_{1.8}S + CuS$[a]	Nanoparticles	/
$PbCl_2 + Tu$	0.5	PbS	Nanoparticles	5-0592
$Pb(NO_3)_2 + Tu$	0.5	PbS	Nanoparticles	5-0592
$AgCl + Tu$	0.5	Ag_2S	Nanoparticles	14-0072
$AgNO_3 + Tu$	0.5	Ag_2S	Nanoparticles	14-0072
$InCl_3 \cdot 4H_2O + Tu$	2	In_2S_3	Nanoflakes	25-390
$FeCl_3 \cdot 6H_2O + Tu$	1.5	Fe_3S_4	Nanoparticles	16-0713

[a] Trace product.

Fig. 1a is the XRD pattern of the formation of NiS using $NiCl_2 \cdot 6H_2O$ and thiourea as the reactants in glycol for 1.5 h. All the peaks can be indexed to hexagonal phase NiS with lattice parameters $a = 3.416$ Å, $c = 5.23$ Å, which are consistent with the reported data ($a = 3.420$ Å, $c = 5.300$ Å, JCPDS Card No. 75-0613). No impurities such as Ni, NiO_x or intermediary phase nickel sulfides are detected in the XRD pattern. According to Scherrer's formula, the average size of the prepared NiS is about 25 nm. Fig. 1b is the corresponding TEM image of obtained sample. It can be seen that the sample consists of nanoparticles of about 35 nm in diameter.

The formation of pseudo-cubic-phase $Cu_{1.8}S$ crystalline is confirmed by the XRD pattern shown in Fig. 2a. According to Scherrer's formula, the average size of $Cu_{1.8}S$ is about 65 nm. Its TEM image is shown in Fig. 2b. It reveals that this sample consists of uniform spherical particles with a size ranging from 40 to 120 nm. In our experiment, different metal salts resulted in different products. If CuCl was used as metal source, the product was $Cu_{1.8}S$, while $CuSO_4 \cdot 5H_2O$ and $Cu(NO_3)_2 \cdot 4H_2O$ resulted in the mixture of CuS and $Cu_{1.8}S$ with different proportions. In this polyol process, we also found that the crystallization water does not have effect on the final product. But if distilled water was introduced, the product was the mixture of copper sulfides and copper oxides.

Fig. 3a is the XRD pattern of produced PbS using $PbCl_2$ as the metal source. All peaks in this figure can be indexed to PbS with cubic cell. After refinement, the lattice parameter is $a = 5.904$ Å, it consists with the reported data (JCPDS Card, No. 5-592). The XRD pattern of the sample using $Pb(NO_3)_2$ as the metal source with no changes of the other conditions is shown in Fig. 3b, which also indicates the formation of PbS. However, the phases and morphologies of these two samples are the same, which agree with the similar XRD

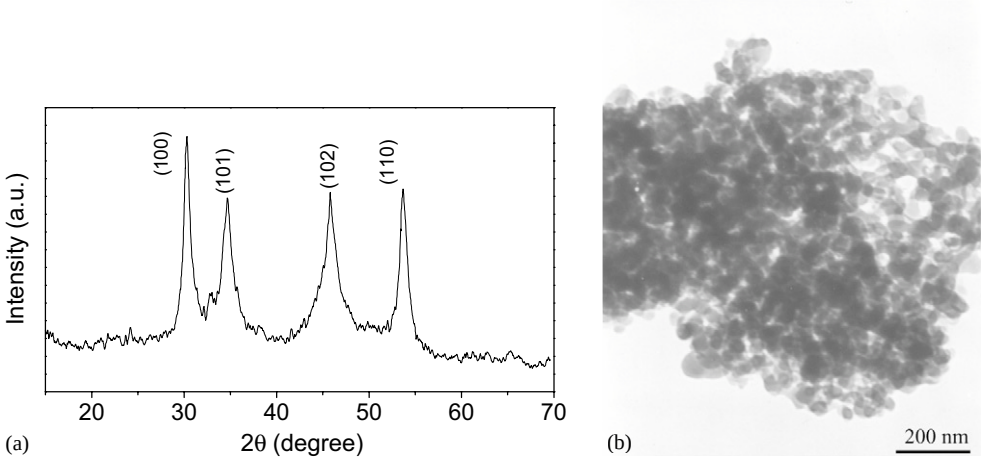

Fig. 1. (a) XRD pattern of NiS; (b) TEM image of NiS.

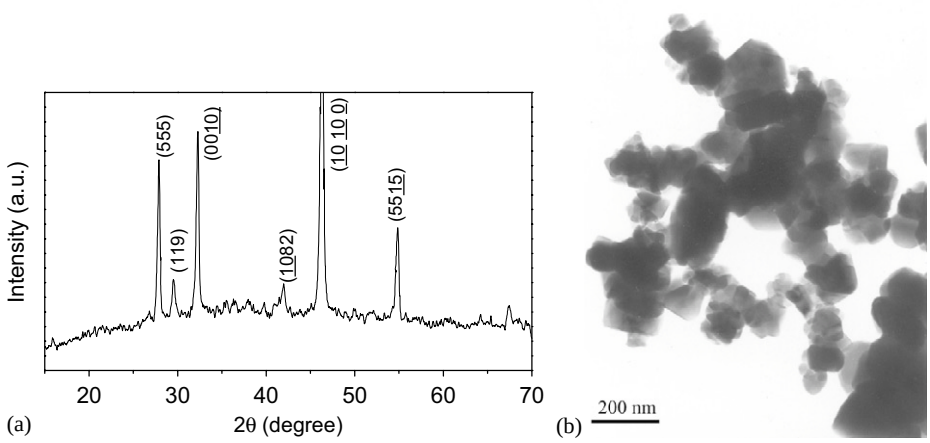

Fig. 2. (a) XRD pattern of $Cu_{1.8}S$; (b) TEM image of $Cu_{1.8}S$.

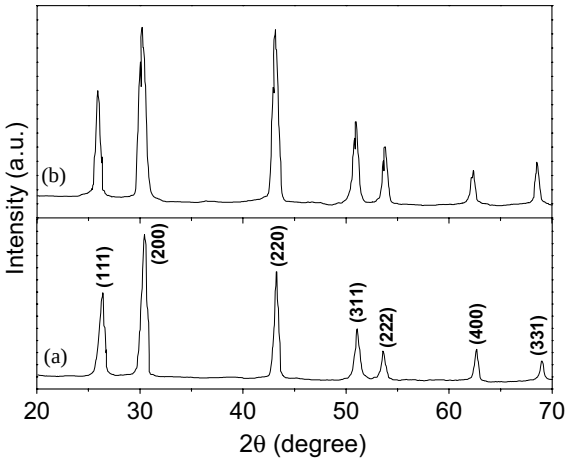

Fig. 3. XRD patterns of PbS (a) obtained from $PbCl_2$; (b) obtained from $Pb(NO_3)_2$.

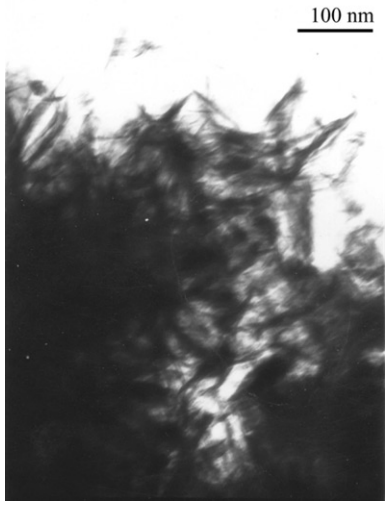

Fig. 4. TEM image of In_2S_3.

patterns. TEM observation shows the average size of PbS is about 50–120 nm.

Besides the nanoparticles, nanoscale crystallines with flaky morphology can also be prepared in the present route. Fig. 4 is the TEM image of the obtained In_2S_3, which reveals the flaky morphology with many irregular drapes on nanometer scale.

EDX analysis was also used to determine the composition of these products. Typical EDX pattern of as-obtained PbS sample is shown in Fig. 5. The results show that the PbS nanoparticles are composed of the elements Pb and S and the ratio of Pb:S is 1:1.07, in agreement with the expected value (the Cu peaks arise from the copper grid). EDX analyses of other products have the similar results, which are also in good agreement with the expected values of final products.

In the polyol method, the polyol used has great effect on the final products. For comparison, different polyols are tested. The results reveal that the viscosity and boiling point of polyol play an important role and the

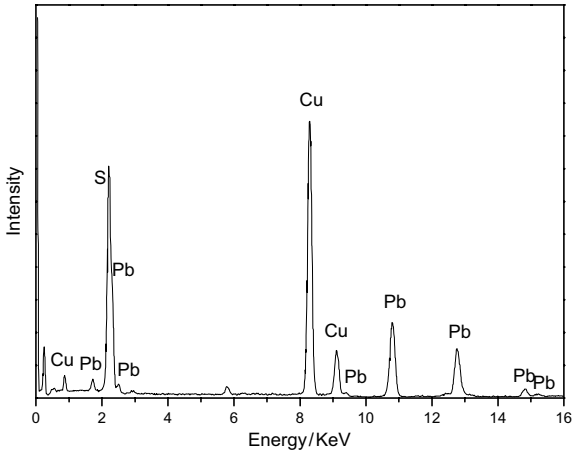

Fig. 5. EDX spectrum of the PbS sample.

better one is glycol. During the experiment, the glycol provides a uniform reaction temperature and makes the reactants mix homogeneously, which is important to the

formation of the homogeneously distributed nanoscale crystallines.

In the synthetic process for binary metal sulfides, when metal salts mixed with thiourea in glycol, metal–thiourea complexes can form according to the literature [18,19]. In the present route, the relatively high solubility of metal salts and thiourea in polyol solution and the change of solution color also reveal the strong complex action between metal ions and thiourea. So the formation of nanoscale metal sulfides crystallines in glycol may be through the following steps: first, metal ions can combine with thiourea molecules to form metal–thiourea complexes in the solution. Second, at a given temperature, the stability of metal–thiourea complexes decreases and undergoes thermal decomposition to form metal sulfides. Meanwhile, it is well known that the thiourea takes part in the following reversible decomposition reaction in solution [20,21]:

$$NH_2CSNH_2 \leftrightarrow CH_2N_2 + H_2S. \quad (1)$$

The formed CH_2N_2 reacts with H_2O at high temperature to produce NH_3 and CO_2 [22]:

$$CH_2N_2 + H_2O \leftrightarrow NH_3 + CO_2. \quad (2)$$

So the decomposition of NH_2CSNH_2 can be expressed as

$$NH_2CSNH_2 + H_2O \leftrightarrow NH_3 + CO_2 + H_2S. \quad (3)$$

Where the trace water (coming from analytical polyol or hydrated metal salts in our experiments) plays a critical role in the formation of metal sulfides crystals, since it can promote the decomposition of NH_2CSNH_2 and the formation of metal sulfides. Actually, during the experimental operations, it is very difficult to avoid the trace water. Based on the above analysis and the results of our experiments, the trace water in analytical polyol or the crystal waters in metal salts is favorable for the further reactions, which is similar to the role of trace water in preparing InAs reduced by zinc powders [23].

Although an extended study of this simple method is needed, we believe that many other binary metal sulfides not listed in Table 1 and some ternary sulfides can also be prepared by using this method. Substituted thiourea with appropriate selenium and tellurium sources, this process in principle can be used to synthesize metal selenides and tellurides. Given the generality of this method, coating and modification of the surfaces may also be fulfilled and additional researches are in progress.

4. Conclusions

In conclusion, a simple polyol method was developed to synthesize metal sulfides nanocrystallines. The key features of this method are the broad applicability and the opportunity to produce nanoscale and crystalline sulfides at moderate temperatures.

Acknowledgments

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