

# A Simple Method for the Preparation of Nanocrystalline Transition Metal Sulfides

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**In this report, many nanocrystalline transition metal sulfides were synthesized through a simple novel reaction between metal salts and sulfur powders under solvothermal conditions at low temperature. The products were characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). Some factors important for the formation of the product and their morphologies are discussed.** © 1999 Academic Press

**Key Words:** transition metal sulfides; nanocrystallines; solvothermal synthesis; disproportionation reaction.

## INTRODUCTION

The variation of a material's properties with size, form of aggregation, and dimensionality has been well known (1). The development of new methods for the preparation of nanostructures is important in both meso- and nanoscale research because the creation of these structures will extend studies of potentially interesting physical phenomena (2). Currently, experimental studies have focused on the preparation and the characterization of solid-state nanometer-scale structures, especially semiconductor nanocrystals (3).

Sulfides of many transition metals show interesting electrical and optical properties such as semiconductivity and photoconductivity (4). For example, silver sulfide is a good prospective photoelectric and thermoelectric material (5), zinc sulfide is one of the most attractive materials for many IR optical applications (6), and nickel sulfide can be used in hydrodesulfurization processes (4). A wide variety of techniques, including solid-state reaction, homogeneous precipitation, gas-phase reaction with H<sub>2</sub>S or sulfur vapor, sol-gel process, electrolysis of thiosulfate solution, spray-pyrolysis method, and microwave irradiation, have been used for the preparation of crystalline sulfides, which require some combination of high temperature, long reaction time, and special apparatus (4, 6–10). The synthesis of metal sulfide nanocrystallites under milder conditions is of interest in both basic research and engineering applications. Recent

efforts to prepare metal sulfides were focused on using organometallic precursors as the reactants at low temperature (11–15); however, the difficulty of the synthesis of the organometallic precursors limits the application of this method. The solvothermal synthesis technique as a newly developed method has been attracting more and more interest due to the controllability of particle morphology and the narrow size distribution (16). In this paper we propose a one-step solvothermal disproportionation reaction that can be used for the preparation of many transition metal sulfides. In a typical experiment, a transition metal chloride, nitrate, or sulfate and sulfur powder were used as the reactants. The synthetic reaction was carried out in an autoclave with an organic compound as the solvent. In this solvothermal process, the disproportionation of S may be the critical factor for the formation of nanocrystalline sulfides. Changing the experimental conditions such as the reactants or the solvent can result in nanocrystallites with different morphology.

## EXPERIMENT

Analytically pure metal chloride, nitrate, or sulfate and an excess of S powders were put in an autoclave of 50-ml capacity that was filled with an organic solvent such as benzene, absolute alcohol, and ethylenediamine up to 85% of the total volume. The autoclave was maintained at 120°C for 12 h and then naturally cooled to room temperature. After filtering and washing with distilled water and absolute alcohol, respectively, the final product was collected.

The product phase was determined from powder X-ray diffraction (XRD) patterns recorded on a Rigaku Dmax $\gamma$ A X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The morphology of the final product was observed by transmission electron microscopy (TEM) operating on a Hitachi H-800 transmission electron microscope.

## RESULTS AND DISCUSSION

The XRD pattern given in Fig. 1a confirms the formation of Ag<sub>2</sub>S using AgNO<sub>3</sub> and S as the reactants in

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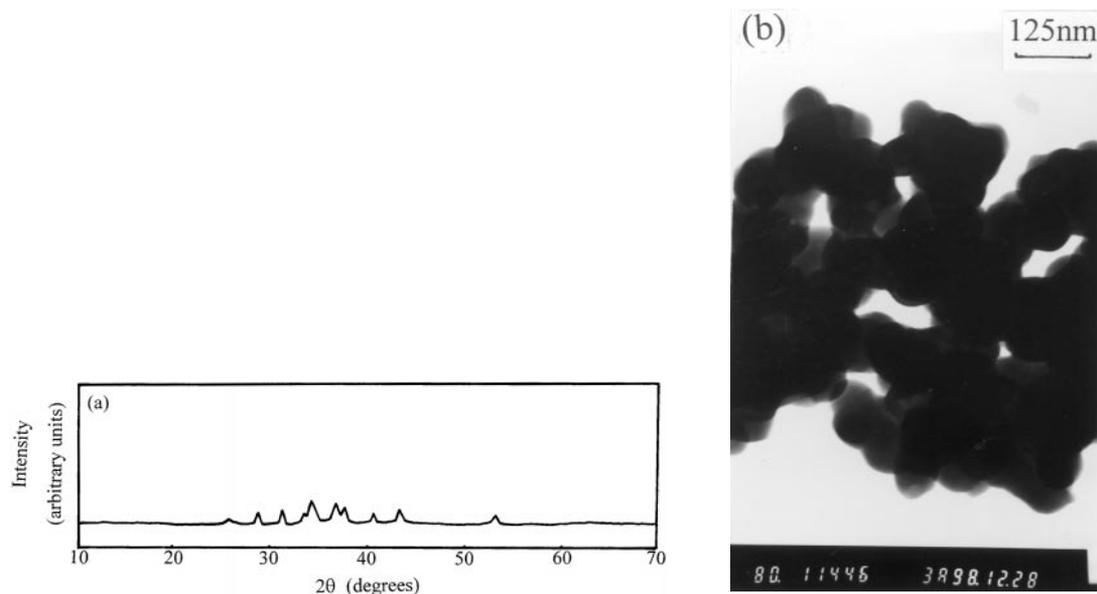


FIG. 1. (a) XRD pattern of the sample  $\text{Ag}_2\text{S}$  prepared in ethylenediamine. (b) TEM image of the sample  $\text{Ag}_2\text{S}$  prepared in ethylenediamine.

ethylenediamine at room temperature (at about  $20^\circ\text{C}$ ). According to Scherrer's formula, the average size of the prepared  $\text{Ag}_2\text{S}$  is about 50 nm. Figure 1b reveals that this sample consists of uniform spherical particles with a size ranging from 50 to 80 nm. Notice that the reaction between  $\text{AgNO}_3$  and S in ethylenediamine is very rapid and would catch fire at room temperature soon after the reactants were put into ethylenediamine. However, in benzene this does not happen and the synthetic reaction between  $\text{AgNO}_3$  and S in benzene was moderate and resulted in the uniform  $\text{Ag}_2\text{S}$  particles with relatively small grain size. Sub-

stituting  $\text{AgCl}$  for  $\text{AgNO}_3$  in ethylenediamine also produced  $\text{Ag}_2\text{S}$  with a slow reaction rate due to the moderating coordination between  $\text{AgCl}$  and ethylenediamine.

The formation of crystalline  $\text{NiS}_2$  is confirmed by the XRD pattern shown in Fig. 2a. Its lattice parameter is calculated to be  $5.677 \text{ \AA}$ , which corresponds to the reported value ( $a = 5.670 \text{ \AA}$ , JCPDS card, No. 11-99). According to Scherrer's formula, the average size of  $\text{NiS}_2$  sample is about 140 nm, which is consistent with the TEM result. (The TEM image of the  $\text{NiS}_2$  is shown in Fig. 2b.)

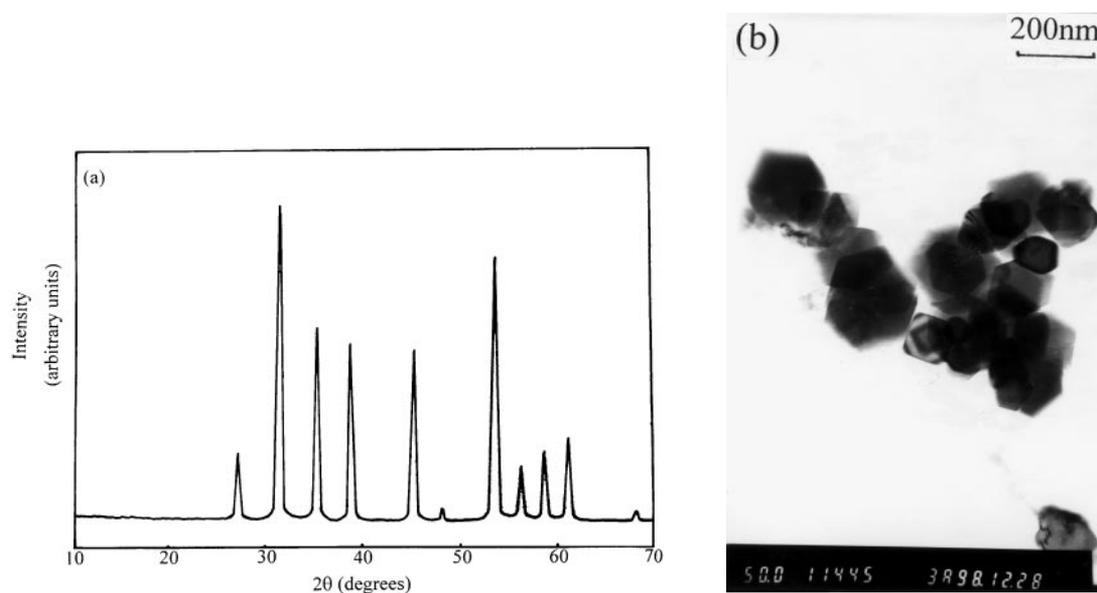
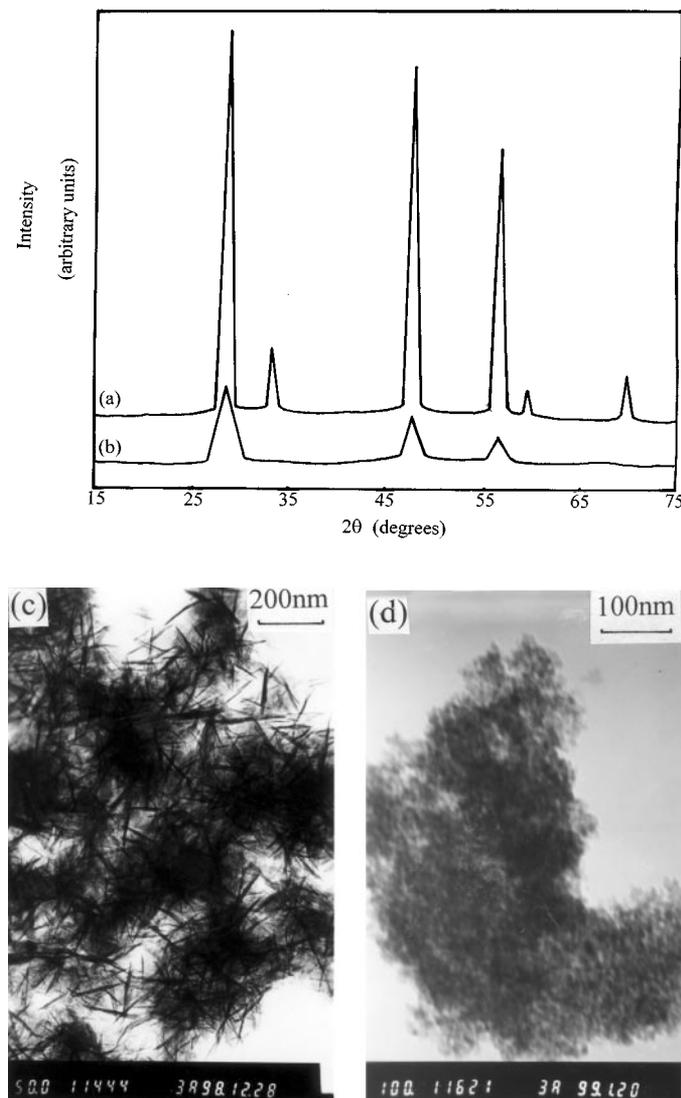


FIG. 2. (a) XRD pattern of the sample  $\text{NiS}_2$  prepared in ethylenediamine. (b) TEM image of the sample  $\text{NiS}_2$  prepared in ethylenediamine.



**FIG. 3.** (a) XRD pattern of the sample ZnS prepared in ethylenediamine. (b) XRD pattern of the sample ZnS prepared in benzene. (c) TEM image of the sample ZnS prepared in ethylenediamine. (d) TEM image of the sample ZnS prepared in benzene.

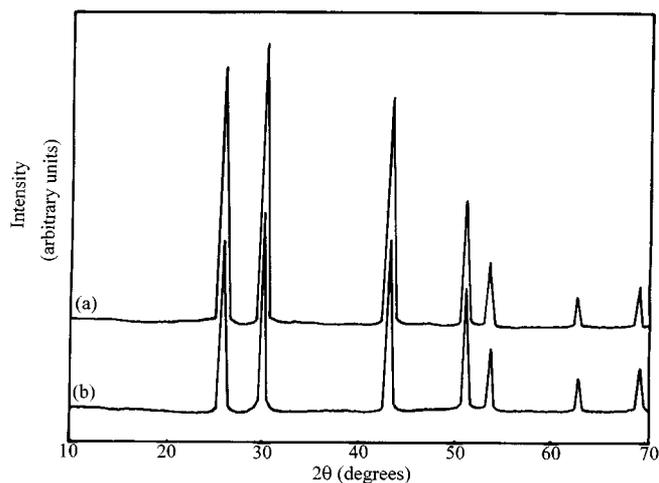
Figures 3a and 3b give the XRD patterns of samples prepared using  $\text{ZnCl}_2$  and S as the reactants in ethylenediamine and benzene, respectively. All peaks in these figures can be indexed to wurtzite ZnS. However, the intensity and broadening of the corresponding peaks in these two figures are quite different, which can be attributed to the different morphologies of the two samples. The average size of the sample prepared in benzene is calculated to be 6 nm from Scherrer's formula. Figures 3c and 3d show the TEM images of these two samples. The sample prepared in ethylenediamine consists of needle-like particles with an axis ratio of 10, whereas the morphology of the sample prepared in benzene is spherical with an average size of 7 nm. This phenomenon can be explained by the effect of different

solvents (16). The ethylenediamine molecule has strong coordinating capability and may act as a bidentate ligand in sulfur-solvent solution to form a relatively stable complex which is prone to form rod-like particles with increasing temperature (17, 18).

Figure 4a shows the XRD pattern of the sample using  $\text{PbCl}_2$  and S as the reactants prepared at  $120^\circ\text{C}$  in ethylenediamine. All peaks in this figure can be indexed to PbS with the cubic cell (JCPDS card, No. 5-592). The XRD pattern of the sample using benzene as the solvent with no changes of the other conditions is shown in Fig. 4b, which also indicates the formation of PbS. However, the morphologies of these two samples are the same, which agrees with the similar XRD patterns. The average size of PbS prepared in ethylenediamine and in benzene is calculated to be 90 and 55 nm, respectively, from Scherrer's formula.

In the solvothermal route, the solvent provides a uniform reaction temperature in the autoclave and makes the reactants mix homogeneously, which is important to the formation of the final uniform nanocrystallites. The different morphologies of PbS and ZnS formed in ethylenediamine indicate the different coordinating capabilities of solvent molecule to  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$ .

In the synthetic process for transition metal sulfides, when metal chlorides and S are used as the reactants, in both ethylenediamine and benzene we could obtain the target products, although the morphologies of the product were different in some cases. So the coordination of ethylenediamine is not the critical factor to the formation of metal sulfides. When benzene was used as solvent, it did not join in the synthetic reaction and just acted as a solvent due to its inactivity. The obtained solid-state product was determined to be metal sulfide and no other impurities could be detected by XRD. So the synthetic reactions might come from the disproportionation of S and the possible by-product was sulfur chloride.



**FIG. 4.** (a) XRD pattern of the sample PbS prepared in ethylenediamine. (b) XRD pattern of the sample PbS prepared in benzene.

**TABLE 1**  
**The Reactants, Experimental Conditions, and Corresponding Products**

Reactants	Proceeding temperatures	Solvents	Reactive time	Products
MnSO <sub>4</sub> · H <sub>2</sub> O + S	120°C	ethylenediamine	12 h	α-MnS
MnCl <sub>2</sub> · 4H <sub>2</sub> O + S	120°C	ethylenediamine	12 h	α-MnS
ZnCl <sub>2</sub> + S	100°C	ethylenediamine	12 h	ZnS (wurtzite)
ZnCl <sub>2</sub> + S	100°C	benzene	12 h	ZnS (wurtzite)
Cd(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O + S	100°C	ethylenediamine	12 h	CdS
CdCl <sub>2</sub> · 2.5H <sub>2</sub> O + S	120°C	ethylenediamine	12 h	CdS
NiCl <sub>2</sub> · 6H <sub>2</sub> O + S	100°C	ethylenediamine	12 h	NiS <sub>2</sub>
AgNO <sub>3</sub> + S	room temperature	ethylenediamine	12 h	β-Ag <sub>2</sub> S
AgNO <sub>3</sub> + S	120°C	absolute alcohol	12 h	β-Ag <sub>2</sub> S
AgNO <sub>3</sub> + S	120°C	benzene	12 h	β-Ag <sub>2</sub> S
AgCl + S	120°C	ethylenediamine	12 h	β-Ag <sub>2</sub> S
CuCl + S	120°C	ethylenediamine	12 h	Cu <sub>2</sub> S
CuCl <sub>2</sub> · 2H <sub>2</sub> O + S	120°C	ethylenediamine	12 h	Cu <sub>x</sub> S
PbCl <sub>2</sub> + S	120°C	ethylenediamine	12 h	PbS
PbCl <sub>2</sub> + S	120°C	benzene	12 h	PbS

The details of the synthetic conditions of the metal sulfides and the corresponding products by this method have been listed in Table 1.

Although an extended study of this method is needed, we believe that many other transition metal sulfides not listed in Table 1 can also be prepared by using this method. In consideration of the disproportionation of Se, this process in principle can be used to synthesize transition metal selenides. Moreover, by changing the experimental conditions such as the solvent, the reaction temperature, and reactants, the morphologies of the final products can be well controlled.

### CONCLUSION

In this report, a simple method was proposed for synthesizing many crystalline transition metal sulfides through a solvothermal process. The formation of these sulfides in a nonpolar solvent such as benzene indicates that the synthetic reaction is determined not by the coordination of the solvent but by the disproportionation of S. Although the coordination of the solvent is not the critical factor to the formation of the nanocrystalline product, it significantly affects the morphology of the final product in some cases.

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