Journal of Solid State Chemistry **161,** 184–189 (2001)
doi:10.1006/jssc.2001.9249, available online at http://www.idealibrary.com on IDEAL®

# A Simple Synthesis of Nanocrystalline Binary Metal Chalcogenides in Alkaline Aqueous Solution

Weixin Zhang,*,† Zeheng Yang,† Juewen Liu,* Yitai Qian,*,[1] Weichao Yu,* Yunbo Jia,*
Xianming Liu,* Guien Zhou,* and Jingsheng Zhu*

**Department of Chemistry and Structure Research Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China; and †School of Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, People's Republic of China*

Received September 12, 2000; in revised form May 2, 2001; accepted May 25, 2001

**Nanocrystalline binary metal chalcogenides have been successfully synthesized through reactions between an alkaline aqueous solution with dissolved elemental S, Se, or Te and an aqueous solution of metal complex at low temperature under atmospheric pressure. The products were characterized by XRD, XPS, TEM, and optical property measurements. Elemental S, Se, and Te dissolved in the alkaline aqueous solution can rapidly make most metal chalcogenides crystallize well. Using metal complex instead of metal ion effectively avoids the occurrence of byproducts such as metal hydroxide or oxide in the alkaline aqueous solution. TEM micrographs show a variety of particle morphologies. The chalcogen sources and solvents are relatively simple and safe. The mechanism of formation of binary metal chalcogenides in the alkaline aqueous solutions is also discussed.** © 2001 **Academic Press**

***Key Words:*** **chalcogen sources; metal complex; binary metal chalcogenides; nanocrystallites; alkaline aqueous solution.**

## INTRODUCTION

Most of the studies of the chemistry of metal selenides and tellurides have been done in the past 20–25 years, in striking contrast to the metal sulfides, which have a long and venerable chemical history, because no convenient synthesis routes, necessary to gain access to the chemistry of metal selenides and tellurides simply, have been available (1–4). Many of the traditional reagents in metal sulfide chemistry, such as $H_2S$, are not simply transferable to their heavier congeners. In the past 10 years, metal selenides and tellurides have begun to assume increasing significance in a variety of important applications, such as in low-band-gap semiconductors, photovoltaics, and IR detectors (5–8). In particular, recent development of nanoscale materials research has induced great interest in its impact on the synthesis methodologies of metal chalcogenides. Knowledge of the chemistry of metal chalcogenides is growing at a rapid rate.

Traditionally bulk metal chalcogenides can be synthesized by solid state reactions between elements at high temperatures for prolonged times (9, 10). These reactions typically produce thermodynamic products with little control of the stoichiometry or crystallinity. In recent literature, the solid state reactions have been accomplished by high-energy ball milling (11), sonochemical (12), or microwave routes (13, 14). New preparation methods, such as synthesis of thin films and nanoparticulates, have concentrated on metal–organic chemical vapor deposition (MOCVD) (15–18), self-propagating high-temperature synthesis (SHS) (19), and solid state metathesis (SSM) synthesis (20). Some methods need organometallic complexes as precursors. Most of these studies involve high energy input.

Because of the lack of suitable entries to the chalcogen sources in aqueous synthesis in air (21, 22), the past 10 years have witnessed a growing interest in nonaqueous synthesis of metal chalcogenides at low temperatures, which involves solubilization of inorganic starting materials such as metals and chalcogen sources (23–26). A range of polar solvents such as methanol, liquid ammonia, amines (ethylenediamine), and *N*,*N*-dimethylformamide (DMF) can disproportionate S, Se, and Te to oxoanions and polychalcogenides $E_x^{2-}$, which can be used as chalcogen sources.

Although it has been known that elemental S, Se, or Te can be dissolved and disproportionated to $E^{2-}$ and $EO_3^{2-}$ ions in NaOH or KOH aqueous solutions in air (27, 28), few reports could be found to synthesize metal chalcogenides based on that result. Herein we choose the alkaline aqueous solutions with dissolved elemental S, Se, or Te as the chalcogen sources, which make most binary metal chalcogenides crystallize well at low temperatures under atmospheric pressure. Previously we have reported that the method can be used to synthesize nanocrystalline $Cu_{2-x}Se$, CdSe, and SnSe in aqueous solution (29–31). Now in this work, the

---

[1] To whom correspondence should be addressed.

0022-4596/01 $35.00

**TABLE 1**
**Characterization of the Chalcogen Sources**

| Elemental alkaline aqueous solution | $E$: $OH^-$ (mol ratio) | $[OH^-]$ (M) | Color |
|---|---|---|---|
| S | 1:130 | 6.5 | Red |
| Se | 1:220 | 11 | Deep red |
| Te | 1:450 | 14 | Deep purple |

method is extended to more systems and the precipitation and reaction parameters are addressed in more details.

## EXPERIMENTAL SECTION

All reagents were of 99.9% purity from Shanghai Chemistry Co. and were used without further purification. Manipulations and reactions were carried out in air. Solution A, which represented the sulfur, selenium, or tellurium (respectively 0.002 mol) alkaline aqueous solution, was prepared according to Table 1. Heating to boiling temperature could accelerate the dissolution of elemental S, Se, or Te in the alkaline aqueous solution. Solution B, which represented the metal complex aqueous solution, was prepared according to the mole ratio of elements in Table 2. A slightly excess (5–10%) of metal salt was dissolved in a ligand aqueous solution such as EDTA or tartaric acid, and a stable metal complex was formed. It should be pointed out that the volume ratio of solution A to B was $\frac{5}{1}$ to $\frac{2}{1}$. Solution B was then added to solution A with rapid stirring. A great amount of precipitate occurred. For the synthesis of PbS, PbSe, $Cu_{2-x}Se$, SnSe, $Ag_2S$, $Ag_2Se$, CdS, and CdSe, the combination proceeded at room temperature. For the synthesis of tellurides and other sulfides and selenides in Table 2, the combination proceeded at 60–140°C for about 10–30 min. After being filtered and washed with distilled water, the precipitate was dried under vacuum at 70°C for 4 h. The final product was collected for characterization.

**TABLE 2**
**X-Ray Powder Diffraction Data of the Products from the Reactions of the Chalcogen Source and Metal Complex**

| Mol ratio of Precursors | Color of product | Product obtained at room temperature | Product obtained at boiling temperature for 10–30 min | JCPDS reference |
|---|---|---|---|---|
| $Pb(CH_3COO)_2$:S 1:1 | Black | PbS | | 5-592 |
| $Pb(CH_3COO)_2$:Se 1:1 | Black | PbSe | | 6-354 |
| $Pb(CH_3COO)_2$:Te 1:1 | Black | | PbTe | 8-28 |
| $SnCl_2$:Se 1:1 | Black | SnSe | | 32-1382 |
| $SnCl_2$:Te 1:1 | Black | | SnTe | 8-487 |
| $Cu(NO_3)_2$:Se 1:1 | black | $Cu_{2-x}Se$ | | 6-680 |
| $CdCl_2$:S 1:1 | Yellow | CdS | | 6-314 |
| $CdCl_2$:Se 1:1 | Red brown | CdSe | | 8-459 |
| $CdCl_2$:Te 1:1 | Black | | CdTe | 15-770 |
| $NiCl_2$:Se 1:1 | Black | | $NiSe_2$ | 11-552 |
| $AgNO_3$:Se 2:1 | Black | $Ag_2Se$ | | 24-1041 |
| $AgNO_3$:S 2:1 | Black | $Ag_2S$ | | 14-72 |
| $Fe(SO_4)_2$:Te 1:1 | black | | $FeTe_2$ | 14-419 |

The X-ray powder diffraction (XRD) pattern was recorded on a MAC Science MXP18AHF X-ray diffractometer with graphite-monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å), employing a sampling width of 0.02° in the $2\theta$ range from 10° to 70°. X-ray tubes were operated with an electron current of 100 mA and a voltage of 40 kV. The XRD patterns were indexed using JCPDS cards. The purity and composition of the product were detected by X-ray photoelectron spectra (XPS) recorded on an ESCALab MKII instrument with Mg $K\alpha$ radiation as the excitation source. The morphology and particle size of crystallites were determined by TEM images and the degree of crystallinity was confirmed by the selected area electron diffraction pattern (ED). The images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution electron microscopy (HREM) images were taken on a JEOL-2010 transmission electron microscope. The photoluminescent (PL) emission spectra of products were performed with a Hitachi 850 fluorescence spectrophotometer with a Xe lamp at room temperature.

## RESULTS AND DISCUSSION

The X-ray powder diffraction (XRD) results showed that the phases and cell constants of as-prepared samples were all close to the values reported in the literature (Table 2) (32). No impurity phase was detected by XRD analysis. The peaks of the samples prepared at room temperature were broadening in comparison with those of samples prepared by heating (Fig. 1). This was in accordance with their small crystalline sizes, which had been confirmed by TEM results. TEM images in Fig. 2 show different morphologies of metal chalcogenides: nearly spheres, plates, cubes, and nanorods. The monodispersity of the crystallites is observed in the samples prepared at room temperature and the polydispersity is often observed in the samples prepared by heating.

The XPS results indicated that the stability of product surface in air decreased in the sequence of metal sulfides, selenides, and tellurides. That is related to the increasing oxidation potentials for these $E^{2-}$ ($E$ = S, Se, or Te) ions ($E°S/S^{2-} = 0.508$ V; $E°Se/Se^{2-} = 0.78$ V; $E°Te/Te^{2-} = 0.92$ V) (33). The XPS analysis indicated that the fresh produced sulfides and selenides had quite high purities. Figure 3 shows XPS analysis of nanocrystalline $Ag_2Se$. The C1$s$ line of carbon contamination appears at 284.8 eV. The two strong peaks at 367.8 eV and 373.85 eV correspond to Ag3$d_{5/2}$ and Ag3$d_{3/2}$ binding energies, respectively. The

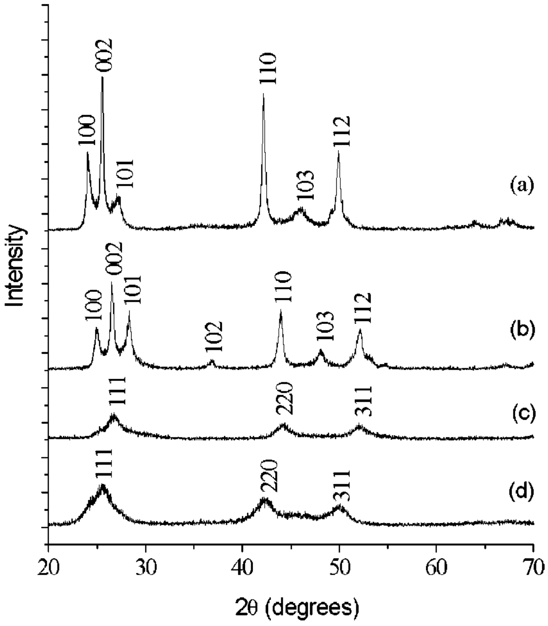

**FIG. 1.** XRD patterns of hexagonal nanocrystalline CdSe (a, c) and CdS (b, d) prepared at boiling temperature and room temperature, respectively.

binding energy of Se3*d* is 53.65 eV. The photoelectron emission arising from elements or oxides is not obvious. This result is close to that of bulk $Ag_2Se$ (34). The contents of Ag and Se are quantified by $Ag3d_{5/2}$ and Se3*d* peak areas and an average composition of $Ag_{2.2}Se$ is given.

The excitation spectrum and photoluminescence (PL) spectrum of hexagonal CdS nanocrystallites with an average particle size of 4 nm are shown in Fig. 4. The excitation spectrum with emission wavelength at 447 nm shows absorption bands at 260 and 378 nm. Under excitation wavelength at 378 nm with a 430-nm filter, the PL spectrum shows an intense, sharp peak at 447 nm with a shoulder peak at 470 nm. The clear appearance of a blue shift of the PL spectrum relative to bulk CdS at 512 nm indicates that the as-prepared hexagonal CdS nanocrystallites are quantum-confined (15). Nanocrystalline hexagonal CdSe has the same appearance and location, but smaller luminescence intensity of the PL spectrum compared with that of hexagonal CdS. There was also a blue shift from the 716 nm bulk band gap in the PL spectrum of hexagonal CdSe nanocrystallites (15).

In our route, the reactions take place as follows:
Dissolution reaction

$$3E + 6\,OH^- \leftrightarrow 2E^{2-} + [EO_3]^{2-} + 3H_2O \qquad [1]$$

$$E^{2-} + (x-1)E \leftrightarrow E_x^{2-} \qquad [2]$$

$$(E = \text{S, Se, or Te})$$

Precipitation reaction

$$E_x^{2-} + [M(\text{edta})]^{2-} \rightarrow ME\downarrow + (x-1)E + (\text{edta})^{4-} \qquad [3]$$

$$E^{2-} + [M(\text{edta})]^{2-} \rightarrow ME\downarrow + (\text{edta})^{4-} \qquad [4]$$

$$(M = \text{Cd, Pb, or Sn}).$$

The reactions of formation of other metal chalcogenides are similar to those described in Eqs. [3] and [4]. The freshly produced elemental S, Se, or Te in Eq. [3] is active and can be dissolved in the excessive alkaline solution at once. Based on the different stabilities of the chalcogen sources, we prepared the related chalcogenides at different temperatures. At room temperature, the sulfur alkaline aqueous solution and the selenium alkaline aqueous solution can be stable only with high $OH^-$ concentrations. Therefore, when they were mixed with the metal complex solutions, PbS, PbSe, $Cu_{2-x}Se$, SnSe, $Ag_2S$, $Ag_2Se$, hexagonal CdS, and CdSe were obtained at room temperature. If the mixtures were heated to boiling temperatures and reacted for about 10–30 min, nanocrystalline $NiSe_2$ was obtained. The crystallite sizes of those prepared at room temperature become larger by heating, which can be observed from TEM images (Fig. 2). The stability of the tellurium alkaline aqueous solution requires not only high $OH^-$ concentrations but also hot conditions (60–140°C). Simply cooling to room temperature will make elemental Te appear on the surface of the solution again because $Te^{2-}$ ion in the solution has a high oxidation potential and is easily oxidized to elemental Te by oxygen in air. CdTe, PbTe, SnTe, and $FeTe_2$ were obtained when the tellurium alkaline aqueous solutions were mixed with the metal complex solutions at 60–140°C. No elemental Te was observed on the surface of the solution or was detected by XRD analysis of the products.

Our experiments showed that if the chalcogen source is in excess, S, Se, or Te will precipitate in the product during posttreatment washing, which can be explained by the reversible reaction of Eq. [1]. Excess S, Se, or Te will be difficult to remove. Therefore, metal complex is in excess (5–10%) over the chalcogen source. At the end of the reactions, excess metal complex can be easily removed by washing with water.

In our method, the chalcogen source has a high concentration of $OH^-$. Table 1 shows that the concentration of S, Se, or Te is much smaller than that of $OH^-$, especially the selenium and tellurium source. If metallic ion is directly used as a reactant, both the metal chalcogenides and the metal hydroxides will precipitate. Metal hydroxides which occur as impurities will be difficult to remove in the posttreatment of the final products.

Chelating agents are often used to prevent one or more of the customary reactions of a metal ion without actually removing it from solution. For example, a metal ion that

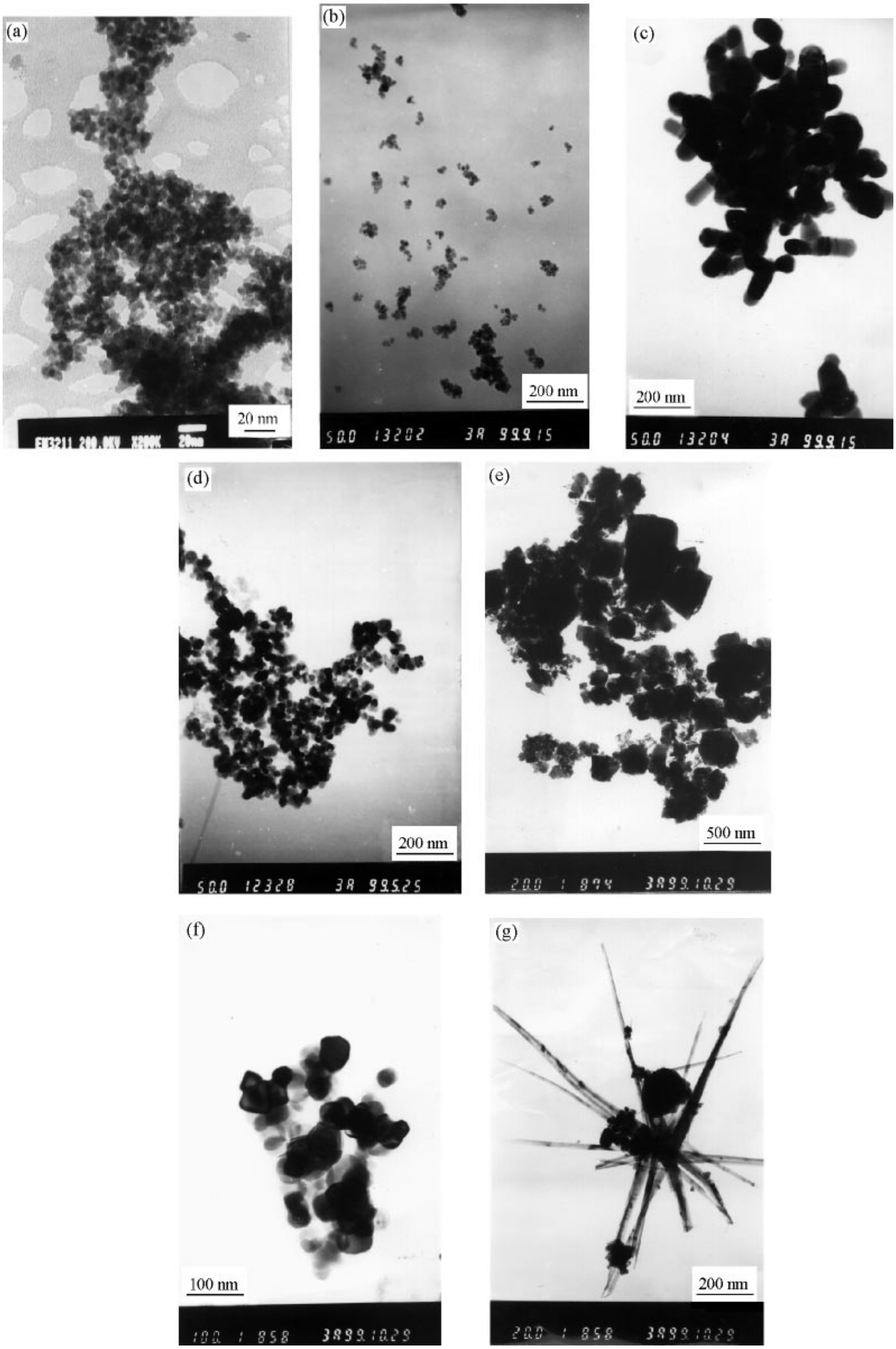

**FIG. 2.** TEM images of typical samples of nanocrystalline metal chalcogenides: (a) CdSe (HREM image) prepared at room temperature, (b) CdS prepared at boiling temperature, (c) CdSe prepared at boiling temperature, (d) CdTe, (e) $NiSe_2$, (f) $Ag_2Se$, and (g) $FeTe_2$.

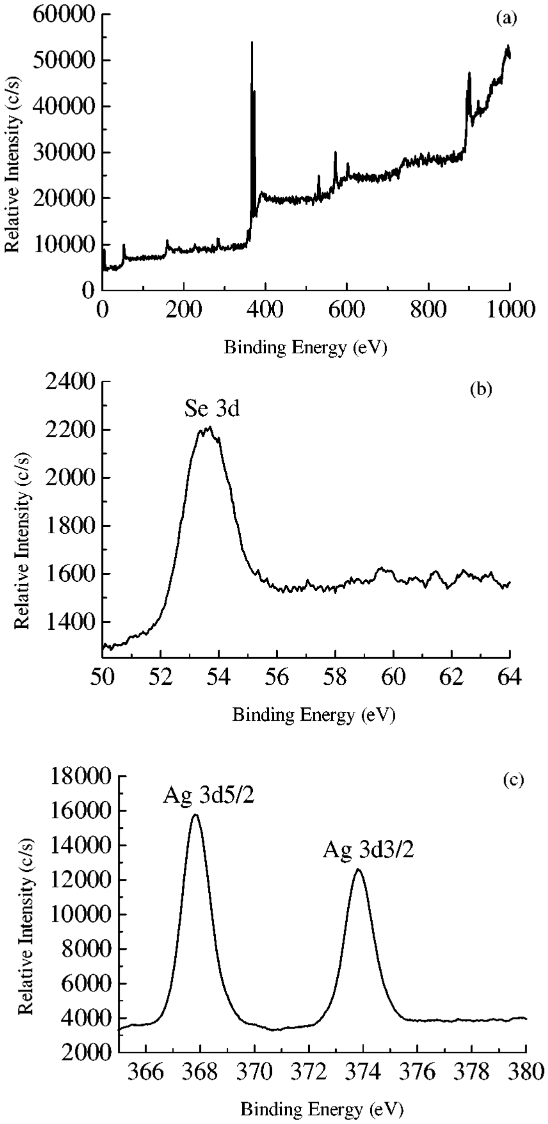

**FIG. 3.** XPS analysis of as-prepared nanocrystalline $Ag_2Se$.

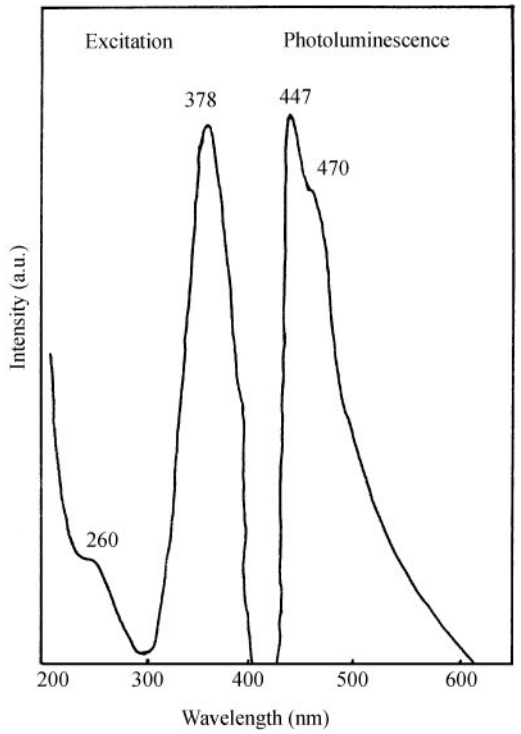

**FIG. 4.** Excitation spectrum (emission wavelength was 447 nm) and photoluminescence spectrum (excitation wavelength was 378 nm, 430 nm filter) of hexagonal nanocrystalline CdS prepared at boiling temperature.

interferes with a chemical analysis can often be complexed and its interference thereby removed. In a sense, the chelating agent hides the metal ion (35). In this method, ligands including chelating agent (EDTA) are used to complex the metal ions. Therefore, the amount of free metal ions in the reaction system is quite small. The solubility product constant of metal chalcogenide will be reached and precipitation will occur before that of metal hydroxide because the solubility product constant of metal chalcogenide prepared in our experiments is much smaller than that of metal hydroxide. In our experiments, using metal complex instead of metal ion avoided the occurrence of metal hydroxides.

Experiments showed that EDTA was a good chelating agent with most metal ions including $Cd^{2+}$, $Pb^{2+}$, $Cu^{2+}$, $Sn^{2+}$, and $Ni^{2+}$, while $S_2O_3^{2-}$ and $NH_3$ were good ligands with $Ag^+$ for formation of $Ag_2S$. However, $[Ag(S_2O_3)_2]^{3-}$ was much more suitable than $[Ag(NH_3)_2]^+$ for formation of $Ag_2Se$. $[Ag(NH_3)_2]^+$ as a silver precursor only produced elemental silver in the selenium alkaline solution, because the stability constant of $[Ag(S_2O_3)_2]^{3-}$ ($\beta = 10^{13.46}$) is much bigger than that of $[Ag(NH_3)_2]^+$ ($\beta = 10^{7.23}$) and silver ion complexed by $(S_2O_3)^{2-}$ is more easily stabilized in the $+1$ oxidation state in the selenium alkaline solution, which has a higher reductivity than the sulfur alkaline solution. Therefore, it is important to choose a ligand which can stabilize the metal ion in the reductive alkaline solution.

## CONCLUSION

In summary, we report a simple synthesis of nanocrystalline metal chalcogenides in alkaline aqueous solution. S, Se, and Te alkaline aqueous solutions are chosen as the chalcogen sources, which make metal chalcogenides crystallize well at low temperature under atmospheric pressure. Using metal complex instead of metal ion effectively avoids the occurrence of byproducts such as metal hydroxide or oxide in alkaline aqueous solution. The precursors and solvents are relatively simple and safe. The convenient synthesis is helpful to gain access to the chemistry of the metal chalcogenides and related nanocrystalline materials. Based on the simple route, synthesis of nanocrystalline materials with controlled morphologies is in progress.

## ACKNOWLEDGMENTS

This work is supported by the Anhui Provincial Foundation of Natural Science (00045112) and the Chinese National Foundation of Natural Science Research and Climbing Program Research-National Foundation Project.

## REFERENCES

1. M. Draganjac and T. B. Rauchfuss, *Angew. Chem., Int. Ed. Engl.* **24,** 272 (1985).
2. A. Müller, E. Diemann, R. Jostes, and H. Bögge, *Angew. Chem., Int. Ed. Engl.* **20,** 934 (1981).
3. A. Müller and E. Diemann, *Adv. Inorg. Chem.* **31,** 89 (1987).
4. D. Coucouvanis, A. Hadjikyriacou, M. Draganjac, M. G. Kanatzidis, and O. Ileperuma, *Polyhedron* **5,** 349 (1986).
5. N. N. Greenwood and E. A. Earnshaw, "Chemistry of the Elements," p. 1403, Pergamon, Oxford, 1990.
6. G. Q. Yeo, H. S. Shen, E. D. Honig, R. Kershaw, K. Dwight, and A. Wold, *Solid State Ionics* **24,** 249 (1987).
7. R. H. Bube, *Annu. Rev. Mater. Sci.* **20,** 19 (1990).
8. A. J. Strauss, *in* "Concise Encyclopedia of Semiconductry Materials and Related Technologies" (S. Mahajan and L. C. Kimerling, Eds.), p. 427, Pergamon, New York, 1992.
9. N. Yellin and L. Ben-Dor, *Mater. Res. Bull.* **18,** 823 (1983).
10. R. Coustal, *J. Chim. Phys.* **38,** 277 (1958).
11. T. Ohtani, K. Maruyama, and K. Ohshima, *Mater. Res. Bull.* **32,** 343 (1997).
12. T. Ohtani, T. Nonaka, and M. Araki, *J. Solid State Chem.* **138,** 131 (1998).
13. D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.* **20,** 1 (1991).
14. K. J. Rao, B. Vaidhyanathan, M. Ganguli, and P. A. Ramakrishnan, *Chem. Mater.* **11,** 882 (1999).
15. C. B. Murray, D. J. Norris, and M. G. Bawendi, *J. Am. Chem. Soc.* **115,** 8706 (1993).
16. A. L. Seligson and J. Arnold, *J. Am. Chem. Soc.* **115,** 8214 (1993).
17. X. Song and M. Bochmann, *J. Chem. Soc., Dalton Trans.* 2689 (1997).
18. M. Green and P. O'Brien *Chem. Commun.* 2235 (1999).
19. H. C. Yi and J. J. Moore, *J. Mater. Sci.* **25,** 1159 (1990).
20. I. P. Parkin, *Chem. Soc. Rev.* **25,** 199 (1996).
21. H. C. Metcalf, J. E. Williams, and J. F. Caskta, "Modern Chemistry," p. 54, Holt, Reinhart, Winston, New York, 1982.
22. R. J. Bandaranayake, G. W. Wen, J. Y. Lin, H. X. Jiang, and C. M. Sorensen, *Appl. Phys. Lett.* **67,** 831 (1995).
23. W. S. Sheldrich and M. Wachhold, *Angew. Chem., Int. Ed. Engl.* **36,** 206 (1997).
24. Y. Li, Z. Wang, and Y. Ding, *Inorg. Chem.* **38,** 4737 (1999).
25. W. Wang, Y. Geng, P. Yan, F. Liu, Y. Xie, and Y. Qian, *J. Am. Chem. Soc.* **121,** 4062 (1999).
26. G. Henshaw, I. P. Parkin, and G. A. Shaw, *J. Chem. Soc., Dalton. Trans.* 231 (1997).
27. "Gmelin Handbook of Inorganic Chemistry" (G. Kirschstein, G. Czack, D. Koschel, and H. K. Kugler, Eds.), 8th ed., Tellurium Supplement Vol. A2, p. 386, Springer-Verlag, Berlin, Heidelberg, 1983.
28. Z. Sh. Karaev, I. O. Nasibov, Sh. A. Alieva, and U. E. Bagirova, *Azerb. Khim. Zh.* **1,** 125 (1962).
29. W. Zhang, X. Zhang, L. Zhang, J. Wu, Z. Hui, Y. Cheng, J. Liu, Y. Xie, and Y. Qian, *Inorg. Chem.* **39,** 1838 (2000).
30. W. Zhang, C. Wang, L. Zhang, X. Zhang, X. Liu, K. Tang, and Y. Qian, *J. Solid State Chem.* **151,** 241 (2000).
31. W. Zhang, Z. Yang, J. Liu, L. Zhang, Z. Hui, W. Yu, Y. Qian, L. Chen, and X. Liu, *J. Cryst. Growth* **217,** 157 (2000).
32. JCPDS Powder Diffraction File, Alphabetical Index, Inorganic Index, Inorganic Phases, 1983.
33. R. C. Weast and M. J. Astle, "CRC Handbook of Chemistry and Physics," 63rd ed., CRC Press, Boca Raton, 1982–1983.
34. C. D. Wagner, W. M. Riggs, L. E. Davis, and J. F. Moulder, "Handbook of X-ray Photoelectron Spectroscopy" (G. E. Muilenberg, Eds.), Perkin-Elmer Corp., Eden Prairie, MN, 1979.
35. "Chemistry: the central science" (T. L. Brown, H. E. Lemay, Jr., and B. E. Bursten, Eds.), 6th ed., p. 927, Prentice Hall, Englewood Cliffs, NJ, 1993.