A Novel "Chemical Scissors" Route to Nanocrystallites

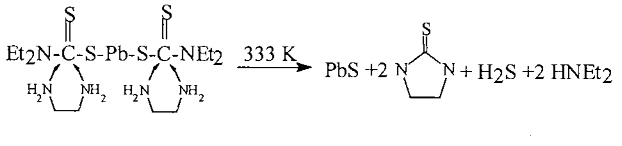
Yi Xie,* Ping Yan, and Yitai Qian
Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China,
Hefei, Anhui 230026, P.R. China

(Received April 1, 1999; CL-990244)

A new strategy, called "chemical scissors" route, utilizing nucleophilic attack to cut the undesired parts off a single-source precursor is proposed, which can significantly reduce the reaction temperature in comparison with simple pyrolysis. As examples, reactions of metal diethyldithiocarbamate (M=Pb, Hg, Cu, Mn, Ag) (acting as the single-source precursor) in ethylenediamine (acting as the scissors and solvent) at 10 – 100 °C result in nanocrystalline MS (M=Pb, Hg, Mn), Ag_2S and $Cu_{1.8}S$.

Reducing the reaction temperatures is always a research goal for both chemists and materialists. High temperatures involved in organometallic chemical vapor deposition (OMCVD) processes can promote interdiffusion of layers and dopants which prevents sharp heterjunctions from being achieved. In the attempts to find processes that would give semiconductors at significantly lower growth temperatures, physical methods such as photo-assisted growth called photoepitaxy,[1] γ-irradiation-assisted preparation,[2] ultrasound-assisted method called sonochemistry,[3] and microwave chemistry[4] were developed. Several chemical methods have also been developed, one involves using reactants with lower bond dissociation energies, for example, $CH_3Te–TeCH_3$ is used to replace $CH_3–TeCH_3$ as tellurium source,[5] a potential drawback for this strategy is the difficulty involved in the purifying and handling of the less stable source. Another promising chemical method is to develop single-source precursors,[6,7] which can offer further advantages such as control over reaction stoichiometry.

In this letter, a new strategy of utilizing nucleophilic attack to cut the undesired parts off a single-source precursor is proposed, and we called it chemical scissors route. We found that the reaction temperature could be significantly reduced in comparison with the simple pyrolysis of the single-source precursor. For example, while 250 °C is required to pyrolyze lead (II) dithiocarbamato complex to prepare PbS films by low-pressure organometallic chemical vapor deposition (OMCVD),[8] 60 °C is high enough for the reaction to complete when ethylenediamine (en) is used as the nucleophiles to attack and cut the thione groups off lead(II) diethyl dithiocarbamate, $Pb(S_2CNEt_2)_2$, as Scheme 1, and the resulting organic product has been characterized in organic chemistry.[9]



Scheme 1.

To metal sulfides there are room temperature routes such as elemental reactions in liquid ammonia or butyl amine,[10] and precipitation of metal cation from aqueous solution by a source of S^{2-},[11] but the products are usually irregular in morphology and agglomerate into particles with diameter in μm scale. In "chemical scissors" route, the reactants are in one phase and the reaction takes place homogeneously, so relatively uniform nanocrystals can be prepared.

In this letter, several nanocrystalline sulfides (PbS, MnS, HgS, Ag_2S, $Cu_{1.8}S$) were prepared by the strategy delineated above. Respective metal diethyl dithiocarbamate ($M(DDTC)_2$, M = Pb, Hg, Cu; $Mn(DDTC)_3$; AgDDTC)[12] (0.5 g) is dissolved in 40 ml ethylenediamine (acting as both solvent and nucleophile), kept in flask at room temperature or heated in autoclave as listed in Table 1. The precipitates were filtered and washed with ethanol and distilled water in sequence. All the products have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) examinations.[13] XRD patterns for the sulfides are shown in Figure 1, which is in agreement with literature.[14] Average crystallite sizes as determined by Scherrer equation[15] based on the XRD linewidths

Table 1. Survey of experimental parameters and results

Reactant	Method[a], Temp/°C,Time	Product	$Size_{XRD}$ /nm [b]	$Size_{TEM}$ /nm [c]
$Pb(DDTC)_2$	A, 60, 6h	PbS	25	23±2
$Hg(DDTC)_2$	R, 10-30, 6h	HgS	14	17±4
$Mn(DDTC)_3$	A, 100, 6h	MnS	20	20±4
$Cu(DDTC)_2$	A, 100, 6h	$Cu_{1.8}S$	20	24±5
AgDDTC	R, 10-30, 12h	Ag_2S	21	18±2

[a] A=autoclave method; R= room temperature. [b] Size determined by Scherrer fomula. [c] Size determined by TEM.

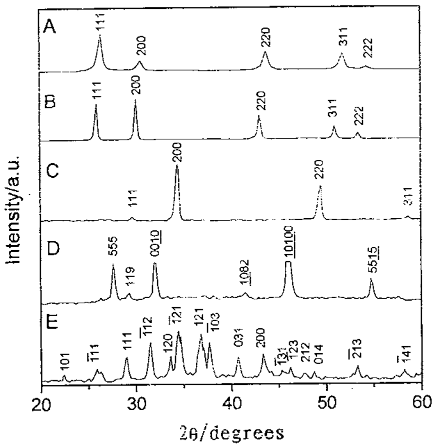


Figure 1. XRD patterns of (A) HgS, (B) PbS, (C) MnS, (D) $Cu_{1.8}S$ and (E) Ag_2S nanocrystals.

are recorded in Table 1. TEM images show nearly monodisperse spherical morphology of the products. As examples, TEM images for PbS and HgS are shown in Figure 2. Particle sizes determined by TEM are also recorded in Table 1, which is in accordance with average size estimated from XRD patterns.

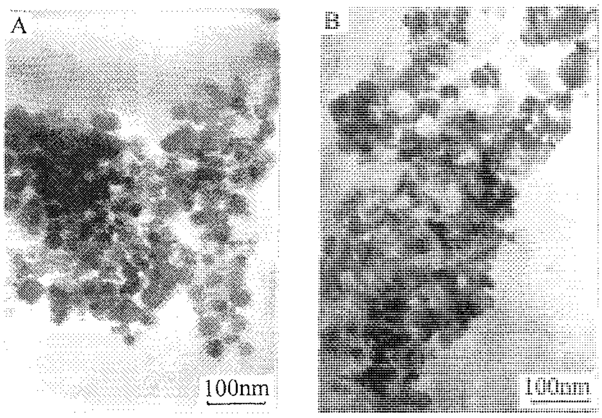


Figure 2. TEM images of (A) PbS and (B) HgS nanocrystals.

Further studies will be extended toward the following two directions: one is to extend this "chemical scissors" to selenides, tellurides, or even phosphides and nitrides; the other is to study whether macromolecules with regularly arrayed amine groups such as polyacrylamide could attack the pecursors to prepare nanowires or regular nanocrystallite arrays.

Financial supports from the Chinese National Foundation of Natural Science Research through the Outstanding Youth Fund and Huo Yingdong Foundation for Young Teachers are gratefully acknowledged.

References and Notes

1 For a review, see M. J. Almond, D. A. Rice, and C. A. Yates, *Chem. Ber.* **24**, 1130(1988).

2 a) Y. J. Zhu, Y. T. Qian, X. J. Li, and M. W. Zhang, *Chem. Commun.*, **1997**, 1081. b) Y. Yin, X. Xu, X. Ge, and Z. Zhang, *Chem. Commun.*, **1998**, 941. c) Y. Yin, X. Xu, X. Ge, and Z. Zhang, *Chem. Commun.*, **1998**, 1641.

3 K. S. Suslick, M. Fang, and T. Hyeon, *J. Am. Chem. Soc.*, **118**, 11960(1996).

4 For a review, see S. A. Galema, *Chem. Soc. Rev.*, **26**, 233(1997).

5 D. W. Kisker, M. L. Steigerwald, T. Y. Kometani, and K. S. Jeffers, *Appl. Phys. Lett.*, **50**, 1681(1987).

6 For reviews, see: a) A. H. Cowley, and R. A. Jones, *Angew. Chem., Int. Ed. Engl.*, **28**, 1208(1989). b) R. L. Wells, *Coord. Chem. Rev.*, **112**, 273(1992). c) A. H. Cowley and R. A. Jones, *Polyhedron*, **13**, 1149(1994).

7 R. D. Culp, A. H. Cowley, A. Decken, R. A. Jones, M. R. Bond, L. M. Mokry, and C. J. Carrano, *Inorg. Chem.*, **36**, 5165(1997).

8 T. Trindade and P. O'Brien, *Chem. Vap. Deposition*, **3**, 75(1997).

9 K. Ramadas and N. Janarthanan, *J. Chem. Res.* (S), **1998**, 228.

10 a) G. Henshaw, I. P. Parkin, and G. Shaw, *Chem. Commun.*, **1996**, 1095. b) G. Henshaw, I. P. Parkin and G. Shaw, *J. Chem. Soc., Dalton. Trans.*, **1997**, 231. c) V. Dusastre, B. Omar, I. P. Parkin, and G. Shaw, *J. Chem. Soc., Dalton. Trans.*, **1997**, 3505.

11 H. C. Metcalf, J. E. Williams, and J. F. Castka. "Modern Chemistry," Holt, Rinehart, Winston, New York (1982), p. 54.

12 $M(DDTC)_2$ were prepared from stoichiometric amounts of aqueous (0.1 mol • L^{-1}) solution of NaDDTC and respective metal salt ($AgNO_3$, $CuCl_2$, $PbAc_2$, $MnCl_2$, $Hg(NO_3)_2$). The precipitate were filtered and washed with deionized water, and dried in vacuum.

13 XRD patterns were obtained on a Japan Rigaku D/Max γA rotation anode X-ray diffractometer with Ni-filtered CuKα radiation (λ=1.54178 Å). TEM measurements were made on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 KV.

14 Joint Committee on Powder Diffraction Standards (JCPDS), File No. 5-592 PbS; 6-261 HgS; 6-518 MnS; 23-962 $Cu_{1.8}S$; 14-72 Ag_2S.

15 H. P. Klug, and L. E. Alexander, "X-Ray Diffraction Procedure for Polycrystalline and Amorphous Materials," 2nd ed, Wiley, New York (1997).