Chem. Mater. 1992, 4, 753–755

Molecular Level Ceramic/Polymer Composites. 3.[1] Synthesis of Polymer-Trapped Cadmium and Copper Sulfides Starting from the Elements and the Structure of the Intermediate, Soluble, Cadmium Sulfide Precursor

Mark E. Wozniak and Ayusman Sen*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry
University of Delaware
Newark, Delaware 19716

Received September 26, 1991
Revised Manuscript Received May 21, 1992

Polymers doped with small semiconductor and conductor clusters represent a new class of materials with novel combinations of properties. Cadmium sulfide (CdS) and copper sulfide (CuS) are two metal sulfides that show such useful properties as photoconductivity and nonlinear optical response.[2] However, in many practical applications, the ability to form films and fibers is an important requirement. This is most easily achieved by forming composites in which the sulfide clusters are embedded in a processable polymeric matrix.[3] A further advantage of synthesizing such composites is that the polymer matrix will physically prevent the agglomeration of the clusters—a persistent problem in size-selective cluster synthesis.

The synthesis of polymer-trapped metal sulfides generally begins with discrete, soluble, precursor compounds that act as sources for the metal ion and the sulfide ion.[3] A synthetic procedure that directly uses the elements would, however, eliminate the need for the preparation of the precursor compounds and would, therefore, be of significant practical advantage. Herein, we report the synthesis of poly(4-vinylpyridine)-trapped CdS and CuS clusters starting *directly* from the respective metallic element and sulfur. Additionally, the structure of the intermediate CdS precursor is described.

Scheme I

M^0 + S_8 + *N*-methylimidazole/poly(4-vinylpyridine)
(M^0 = Cd, Cu)

$$\Big\downarrow \text{MeOH/25 °C}$$

(*N*-methylimidazole)$_n$M$_x$S$_y$/poly(4-vinylpyridine)

$$\Big\downarrow \begin{array}{l}\text{(a) film casting}\\ \text{(b) thermal curing (Cu, 100 °C;}\\ \text{Cd, 160 °C)}\end{array}$$

metal sulfide (CdS or CuS) containing poly(4-vinylpyridine)

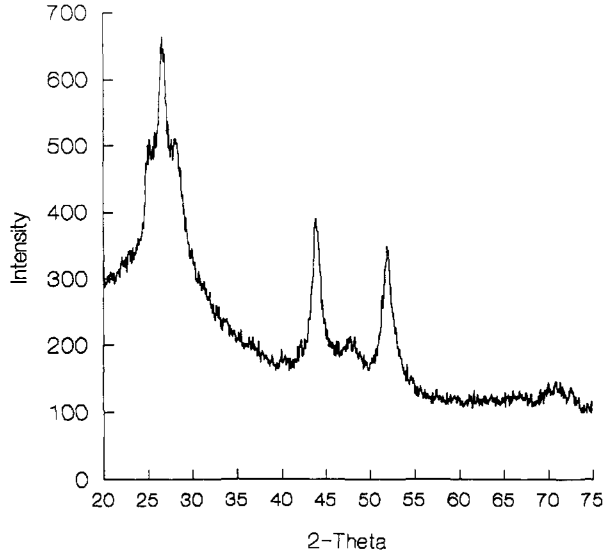

Figure 1. X-ray powder diffraction pattern obtained for CdS formed by the decomposition of the precursor complex in the solid state at 160 °C.

The sequence of steps involved in the synthesis of the polymer-trapped metal sulfide clusters is outlined in Scheme I. In a typical reaction, 6 mmol of Cu or Cd (100–200 mesh), 6 mmol of sulfur, and 30 mmol of *N*-methylimidazole were added to a methanolic solution containing 1.0 g of poly(4-vinylpyridine) (Polysciences, MW = 300000). After this was stirred at 25 °C for several hours under an inert atmosphere, most of the metal and the sulfur had dissolved. Following centrifugation to remove unreacted metal and some precipitated metal sulfide, the solution was used to cast films. The films were subsequently thermally cured by gradually heating them to 100 °C for CuS and 160 °C for CdS, for 12 h under an inert atmosphere. The function of *N*-methylimidazole was to facilitate the dissolution of the metal to form *N*-methylimidazole-coordinated metal polysulfide species, as has been described by Rauchfuss.[4] During thermal curing, *N*-methylimidazole, as well as excess sulfur, was extruded to generate the corresponding metal sulfide. While the formation of the CuS clusters occurred during thermal curing at 100 °C, the Cd-containing films were further heated to 160 °C to complete the formation of CdS.

To confirm that crystalline CdS was formed at the rather low temperature of 160 °C, a solution synthesis was performed. The reaction conditions used for the solution synthesis were identical to those reported above except that 0.76 g of pyridine was employed in place of poly(4-

---

[1] Part 2: Nandi, M.; Conklin, J. A.; Salvati, L.; Sen, A. *Chem. Mater.* **1991**, *3*, 201. Part 1: Nandi, M.; Conklin, J. A.; Salvati, L.; Sen, A. *Chem. Mater.* **1990**, *2*, 772.

[2] Recent references: (a) Yuan, Y.; Fendler, J. H.; Cabasso, I. *Chem. Mater.* **1992**, *4*, 312. (b) Yuan, Y.; Cabasso, I.; Fendler, J. H. *Macromolecules* **1990**, *23*, 3198. (c) Baral, S.; Fendler, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 1604. (d) Zhao, X. K.; Baral, S.; Rolandi, R.; Fendler, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 1012. (e) Haga, Y.; Inoue, S.; Nakajima, M.; Yosomia, R. *Mater. Chem. Phys.* **1988**, *19*, 381. (f) Im, S. S.; Im, H. S.; Kang, E. Y. *J. Appl. Polym. Sci.* **1990**, *41*, 1517. (g) Dannhauser, T.; O'Neil, M.; Johansson, K.; Whitten, D.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 6074. (h) *Nonlinear Optics of Organics and Semiconductors*; Kobayashi, T., Ed.; Springer-Verlag: Berlin, 1988; Part II. (i) Wang, Y.; Suna, A.; McHugh, J.; Hilinski, E. F.; Lucas, P. A.; Johnson, R. D. *J. Chem. Phys.* **1990**, *92*, 6927. (j) Hilinski, E. F.; Lucas, P. A.; Wang, Y. *J. Chem. Phys.* **1988**, *89*, 3435. (k) Wang, Y.; Herron, N.; Mahler, W.; Suna, A. *J. Opt. Soc. Am. B* **1989**, *6*, 808. (l) Cheng, L.-T.; Herron, N.; Wang, Y. *J. Appl. Phys.* **1989**, *66*, 3417. (m) Jain, R. K.; Lind, R. C. *J. Opt. Soc. Am.* **1983**, *73*, 647. (n) Fluegel, B.; Joffre, M.; Park, S. H.; Morgan, R.; Hu, Y. Z.; Lindberg, M.; Koch, S. W.; Hulin, D.; Migus, A. *J. Cryst. Growth* **1990**, *101*, 643. (o) Henneberger, F.; Puls, J.; Rossmann, H.; Woggon, U.; Freundt, S.; Spiegelberg, C.; Schuelzgen, A. *J. Cryst. Growth* **1990**, *101*, 632. (p) Ohashi, Y.; Ito, H.; Hayashi, T.; Nitta, A.; Matsuda, H.; Okada, S.; Nakanishi, H.; Kato, M. *Springer Proc. Phys.* **1989**, *36*, 81. (q) Spanhel, L.; Anderson, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 2278. (r) Pileni, M. P.; Motte, L.; Petit, C. *Chem. Mater.* **1992**, *4*, 338.

[3] Recent references: (a) Reference 2a,b,f,i–k,p. (b) Reference 2h, p 81. (c) Mahler, W. *Inorg. Chem.* **1988**, *27*, 435. (d) Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315. (e) Bianconi, P. A.; Lin, J.; Strzelecki, A. R. *Nature* **1991**, *349*, 315.

[4] (a) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 2514. (b) Dev, S.; Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6385. (c) Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043.

0897-4756/92/2804-0753$03.00/0

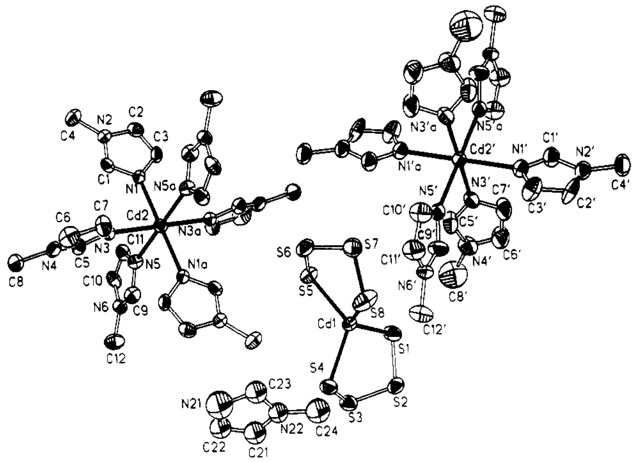

Figure 2. Structure of [Cd(N-methylimidazole)$_6$][Cd(S$_4$)$_2$]·(N-methylimidazole) containing two crystallographically independent, chemically similar, half-occupancy cations. Thermal ellipsoids are drawn at the 35% probability level.

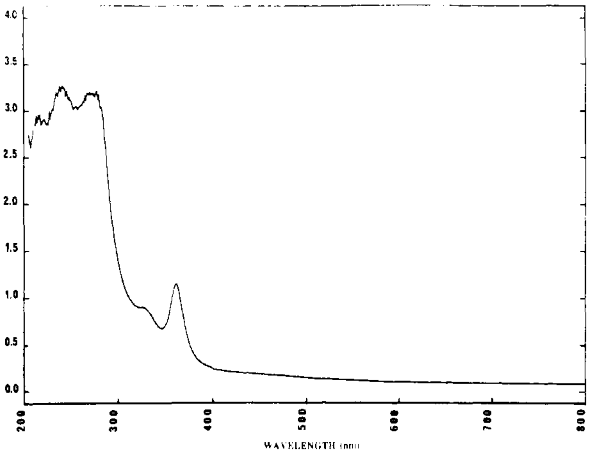

Figure 3. UV–visible spectrum of a CdS-doped poly(4-vinylpyridine) film.

vinylpyridine). After 18 h of stirring at 25 °C, the resultant dark yellow solution was filtered to remove unreacted metal. Long bright yellow crystals could then be isolated from the filtrate by removing the solvent slowly under vacuum (yield 82% based on sulfur). Upon heating under vacuum to 160 °C for 12 h the yellow crystals were converted to a yellow-brown powder. X-ray powder diffraction experiments showed this powder to be crystalline CdS in predominantly the wurtzite form (Figure 1). Elemental analysis of the powder revealed the presence of small amounts of carbon (3.75%), hydrogen (<0.5%), and nitrogen (0.80%). Crystalline CdS was also formed when the precursor species was decomposed in a solution of either N-methylimidazole or in pyridine at 160 °C.

The structure of the intermediate, soluble, CdS precursor obtained from the above synthesis was determined by single-crystal X-ray diffraction.[5] As shown in Figure 2, it is an ionic compound consisting of a Cd(N-methylimidazole)$_6^{2+}$ cation and a Cd(S$_4$)$_2^{2-}$ anion. The crystallographic asymmetric unit contains two half-occupancy cations each located on an inversion center, one anion on a general site, and a molecule of uncomplexed N-methylimidazole. There are no significant interionic or molecular contacts in the lattice. All the bond lengths and angles are unexceptional.

The metal sulfide doped poly(4-vinylpyridine) formed transparent free-standing films upon curing. The CdS containing films were golden yellow, whereas those containing CuS were dark green. The weight percentages of the dopant levels in the films, as obtained by elemental analysis were 1.4% Cd, 1.5% S, and 4.6% Cu, 6.7% S, respectively. The excess sulfur (over that required by stoichiometry for the metal sulfide) was extruded from the metal polysulfide precursor during conversion to the corresponding metal sulfide.[4] Note that the S/Cd molar ratio of 4.0 in the doped films was close to that observed for the precursor complex. Likewise, the S/Cu molar ratio of 2.9 found for the CuS-doped polymer was similar to the value of 2.5 observed for the N-methylimidazole-coordinated copper polysulfide species isolated by Rauchfuss.[4c]

X-ray powder diffraction studies were performed to ascertain the structures of the metal sulfides present in the films. The 2θ measurements confirmed that CuS was present in the form of covellite. However, no diffraction pattern was seen in the case of the CdS-containing films. One explanation for this observation is that the size of the CdS crystallites were significantly smaller than those of CuS and, in fact, were too small to give rise to a sharp X-ray diffraction pattern.[6] Additionally, a poor signal-to-noise ratio was expected due to the low concentration of CdS in the polymeric matrix.

The above supposition was confirmed by measurement of the UV-vis spectra of the doped polymers. For the CuS-doped films, a broad featureless absorption corresponding to bulk conducting CuS was obtained. In the case of CdS-doped films, an absorption edge that was significantly blue-shifted from that of bulk CdS was observed (Figure 3).[7] In addition, prominent fine structures were observed at 332 and 362 nm. According to Brus, Wang, and others, the fine structures are due to discrete exciton transitions, most likely the first and second transitions in the same cluster.[8] Note that only the presence of a narrow cluster size distribution allows the observation of these spectral features. By comparing the position of the absorption edge for the CdS-doped polymers with the calibration curves found in the literature, the average size of the CdS clusters was determined to be 20–30 Å.[8,9] After heating to 190 °C, the UV-vis spectrum of the these films corresponded to that of bulk CdS, thereby indicating that thermally induced agglomeration of the CdS clusters had occurred. The spectral changes corresponding to precursor to nanocluster to bulk CdS conversion in the polymer matrix were also observed in solution when the precursor

---

(5) Crystal data for [Cd(C$_4$H$_6$N$_2$)$_6$][Cd(S$_4$)$_2$]·C$_4$H$_6$N$_2$: monoclinic, $P2_1/n$, a = 8.3203 (14), b = 22.698 (4), c = 23.474 (3) Å, β = 95.097 (13)°, V = 4415.6 (13) Å^3, Z = 4, T = 297 K, $R(F)$ = 5.80% for 3816 observed ($4\sigma F$) reflections, 4° ≤ 2θ ≤ 50°, Mo Kα.

(6) Azarott, L. V.; Buerger, M. J. *Powder Method in X-Ray Crystallography*; McGraw-Hill: New York, 1958; p 255.

(7) The long absorption tail extending to 600 nm that is observed in Figure 3 resulted from the reaction of extruded sulfur with N-methylimidazole and/or poly(4-vinylpyridine). This was verified by a control experiment involving these three species. The fine structural features present in Figure 3 were, of course, absent in the spectrum derived from the control experiment. The formation of colored species by the reaction of sulfur with amines has been reported: Davis, R. E.; Naksbundi, H. F. *J. Am. Chem. Soc.* **1962**, *84*, 2085.

(8) (a) Spanhel, L.; Anderson, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 2278. (b) Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 2555. (c) Brus, L. E.; Rosetti, R.; Nakahara, S. *J. Chem. Phys.* **1983**, *79*, 1086. (d) Wang, Y.; Suna, A.; McHugh, J.; Hilinski, E. F.; Lucas, P. A.; Johnson, R. *J. Chem. Phys.* **1990**, *92*, 6929.

(9) (a) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525. (b) Wang, Y.; Herron, N. *Phys. Rev. B* **1990**, *42*, 7253. (c) Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* **1990**, *112*, 1322. (d) Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Rajh, T.; Micic, O. I. *J. Phys. Chem.* **1985**, *89*, 397. (e) Rosetti, R.; Nakahara, S.; Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 1086. (f) Rosetti, R.; Ellison, J. L.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4464. (g) Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1985**, *82*, 552.

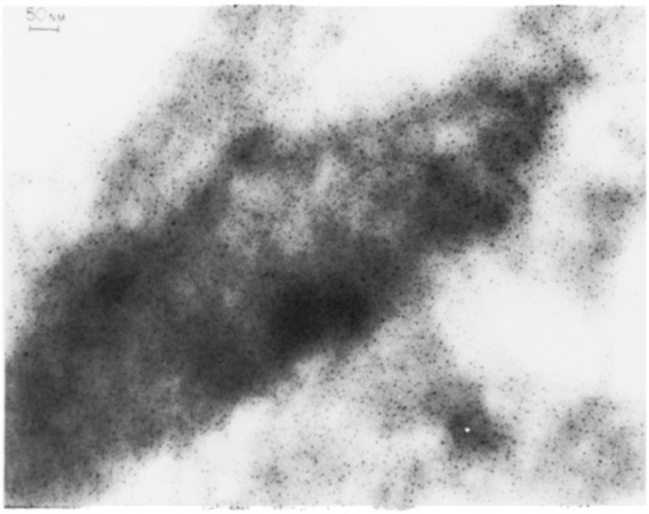

Figure 4. Transmission electron micrograph of a CdS-doped poly(4-vinylpyridine) film. The dark shadows represent microtoming effects and are not part of the composite material.

complex was heated in *N*-methylimidazole at 160 °C. As expected, the rate of particle growth in solution was directly related to the precursor concentration. These observations suggest that the in situ decomposition of the precursor in the polymer followed closely that observed in solution. The only significant difference was that because of "site isolation"[1] (vide infra) formation of bulk CdS through nanocluster agglomeration was not observed in the polymer matrix except at significantly higher temperatures.

The cluster sizes inferred from UV–vis spectroscopy were confirmed by transmission electron microscopy (TEM). For CuS-doped films, particles with sizes ranging from 100 to 450 Å were observed. For films containing CdS, 20–30-Å clusters were observed (Figure 4). Furthermore, these sulfide clusters were distributed uniformly throughout the bulk and the surface of the polymeric films. The latter was confirmed by energy dispersive X-ray analysis of the film surfaces. In addition to the sulfide clusters, large islands (100–1000 Å in size) of elemental sulfur were observed by TEM in CuS-doped samples. These were judged to be composed of amorphous sulfur (as opposed to crystalline CuS) due to the absence of any electron diffraction pattern.

The difference in size between the CuS and CdS clusters is intriguing. This may simply be due to the inherent differences between CuS and CdS. Alternatively, it may be related to the temperature at which the formation of the metal sulfide occurred. The nitrogens on *N*-methylimidazole or poly(4-vinylpyridine) may be expected to coordinate to the metal ions on the surface of the sulfide clusters. The formation of CuS from the corresponding polysulfide species occurred at the same temperature at which the film was cured. At that point, a significant quantity of the high-boiling *N*-methylimidazole was present which would act both as a plasticizer and as a coordinating ligand, thereby allowing the CuS clusters to migrate and agglomerate. On the other hand, CdS was formed at 160 °C, *after* the film was fully cured. At that point *N*-methylimidazole was no longer present and, as a result, the mobility of CdS clusters, as well as the polysulfide precursors, was very limited due to their coordination solely to the pendant pyridine groups on poly(4-vinylpyridine). Thus, the size of the CdS clusters may be defined by the original precursor species and by their inability to migrate. A narrow size distribution may therefore be expected.

The coordination of the nitrogens of poly(4-vinylpyridine) to the surface metal ions of the sulfide clusters in the fully cured doped polymer samples was supported by glass transition temperature (T_g) measurements. If such a coordination was present, a slight increase in T_g would be expected since the sulfide clusters would act as weak intermolecular cross-linking agents. Indeed, the T_g values observed for pure poly(4-vinylpyridine) and the CuS- and CdS-doped poly(4-vinylpyridine) samples were 65, 82, and 87 °C, respectively.

The coordination of the ligating atoms on the polymer to the sulfide clusters resulted in the stabilization of the latter. Thus, there was no discernible change in either the UV–vis spectra or the X-ray powder diffraction pattern after the doped polymers were stored in air for 4–6 months.

In conclusion, we have demonstrated that it is possible to synthesize polymer-trapped metal sulfides starting directly from the respective elements, thus dispensing with the need to independently synthesize the precursor materials. Additionally, under "site-isolation" conditions,[1] it is possible to generate metal sulfide nanoclusters with a relatively narrow size distribution. Such nanoclusters represent a new class of materials with novel properties that are different from those of discrete molecules, as well as bulk solid-state materials.[10]

Acknowledgment. This research was supported by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FG02-84ER13295).

Supplementary Material Available: Tables of crystal, data collection and refinement parameters, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (8 pages); table of structure factor tables (28 pages). Ordering information is given on any current masthead page.

---

(10) Recent reviews: (a) Reference 9a. (b) Steigerwald, M. L.; Brus, L. E. *Acc. Chem. Res.* **1990**, *23*, 183. (c) Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471. (d) Andres, R. P.; Averback, R. S.; Brown, W. L.; Brus, L. E.; Goddard, W. A.; Kaldor, A.; Louie, S. G.; Moscovits, M.; Peercy, P. S.; Riley, S. J.; Siegel, R. W.; Spaepen, F.; Wang, Y. *J. Mater. Res.* **1989**, *4*, 704. (e) Brus, L. J. *Phys. Chem.* **1986**, *90*, 2555.