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# Preparation of Au<sub>2</sub>S<sub>3</sub> and nanocrystalline gold by sonochemical method

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## Abstract

We report a new synthesis of  $Au_2S_3$  by a sonochemical reaction between  $Au(CH_3COO)_3$  and S in decalin at room temperature in nitrogen atmosphere. When gold acetate is sonicated under similar conditions without the presence of sulfur, nanocrystalline gold is formed. The products were characterized by X-ray powder diffraction, transmission electron microscope and thermal analysis (TG and DSC). The synthesis procedure is substantially simpler than the previously reported methods. © 2003 Elsevier B.V. All rights reserved.

Keywords: Sonochemical reaction; Sulfides; Nanostructures

# 1. Introduction

Semiconductor nanoparticles, especially metal chalcogens such as CdS, CdSe, ZnS, PbS and so forth, exhibit dramatic changes in their optical absorption and emission spectra as a function of their size [1] and shape [2]. Despite the fact that metal chalcogen nanoparticles have been extensively studied, there are a limited number of publications concerning the preparation and characterization of gold sulfide nanoparticles, although gold compounds are attractive materials for solid state ionics [3]. The traditional methods [4,5] to synthesize Au<sub>2</sub>S and Au<sub>2</sub>S<sub>3</sub> always used highly toxic H<sub>2</sub>S as the source of sulfur. Gold complexes having the appropriate valence state of gold were used for the preparation of monovalent and trivalent gold sulfide [6]. Au<sub>2</sub>S<sub>3</sub> has been prepared long ago by passing H<sub>2</sub>S over dry lithium tetrachloroaurate [7] or by reaction between  $H_2S$  and an acidified solution of H(AuCl<sub>4</sub>) in absolute ether [8]. More recently, Senfite and Wright prepared trivalent gold sulfide [9] by a reaction between H<sub>2</sub>S and trivalent gold in the form of  $Au_2(SO_4)_3$ , prepared electrolitically in concentrated  $H_2SO_4$ . Au<sub>2</sub>S<sub>3</sub> is a black precipitate that

reacts vigorously with nitric acid and is insoluble in other mineral acids. It reacts with sodium cyanide and concentrated sodium sulfide solutions. The material appears to be amorphous and has no reported X-ray diffraction pattern.

Nanocrystalline gold with particle size up to 20 nm has been prepared by a gas evaporation technique combined with a solvent trap method [10] and recently by gas deposition method onto a glass substrate [11,12]. No reports about use of sonochemical methods for the preparation of either nanocrystalline gold or  $Au_2S_3$  could be found in literature.

Acoustic cavitation, that is the formation, growth and subsequent implosive collapse of gas bubbles in an ultrasonically irradiated liquid, generates a transient localized hot spot with an effective temperature up to 5000 °C and a submicrosecond lifetime [13–15]. The rapid cavitational cooling rate (>10<sup>9</sup> K/s) stabilizes the nanometer-sized clusters produced during the cavitation. Suslick et al. have employed this method for the preparation of nanosized powders of Fe, Co and their alloys [16–18]. Nanostructured sulfides, selenides and tellurides with interesting chemical and physical properties have recently been prepared by the sonochemical route [19–24].

In this paper, we report a simple one-step synthesis of amorphous  $Au_2S_3$  via a sonochemical synthesis from

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 $Au(CH_3COO)_3$  and elemental S in decalin. The preparation of ultrafine gold particles by sonochemical decomposition of  $Au(CH_3COO)_3$  in decalin is also reported.

# 2. Experimental

All reagents were commercial products and were used without further purification.

#### 2.1. Synthesis of $Au_2S_3$

In a typical procedure for the preparation of Au<sub>2</sub>S<sub>3</sub>, sulfur (15.40 mg, 0.481 mmol) has been dissolved in 12 ml of decalin in a Suslick reaction vessel by stirring on a magnetic stirrer for 10 min. Gold acetate, Au(CH<sub>3</sub>COO)<sub>3</sub> (100 mg, 0.267 mmol), was added and the slurry was stirred for another 10 min to obtain better homogenization. Before starting the irradiation, the mixture was outgassed with nitrogen for 15 min. Then the slurry was irradiated for 2 h under nitrogen with high-intensity ultrasound (Sonics & Materials VCX600: 20 kHz, 80 W/cm<sup>2</sup>, 1 cm<sup>2</sup> titanium direct immersion horn) in a cooling bath with a constant temperature of 0 °C. Following the reaction, the obtained black powder was centrifuged, the nearly clear supernatant was decanted and the product was washed first with fresh decalin to remove any unreacted sulfur and then with absolute ethanol to wash out the decalin, and finally air-dried. The products were weighed and the calculated yield, based on the initial mass of Au(CH<sub>3</sub>COO)<sub>3</sub>, is in the range 80-90%.

#### 2.2. Preparation of nanocrystalline gold

A slurry of Au(CH<sub>3</sub>COO)<sub>3</sub>(100 mg, 0.267 mmol) in 12 ml of decalin was prepared in a Suslick reaction vessel, stirred for 15 min, outgassed with nitrogen for 15 min and irradiated with ultrasound as described above. The irradiation time varied from 30 min to 4 h. The black precipitate was centrifuged, washed with absolute ethanol and air-dried.

#### 2.3. Characterization of the products

The products were characterized with an AXS-Bruker/Siemens model D5005 X-ray powder diffractometer (XRD) equipped with a Cu K<sub> $\alpha$ </sub> radiation source and graphite monochromator ( $\lambda = 1.54178$  Å). The thermal analyses (TG and DSC) were done using a Mettler TA4000 system. The morphology and size of the products were observed by transmission electron microscopy (TEM) on a Jeol JXA-840 microscope using an accelerating voltage of 200 kV.

#### 3. Results and discussion

The XRD patterns of the as-prepared precipitates of  $Au_2S_3$  show extremely broad peaks and indicate that the obtained products are amorphous. Attempts to prepare crystalline material by annealing the amorphous product were unsuccessful due to the low thermal stability of  $Au_2S_3$ . Some qualitative properties of the product were established: the compound is soluble in sodium cyanide and reacts with nitric acid, but is insoluble in other mineral acids. To characterize the compound formed, gravimetric analyses were made on the dried product. The compound is thermally stable up to 110 °C and decomposes at higher temperatures, leaving pure metallic gold as a residue at 500 °C. The measured percentage of gold in the product is 80.73%, and is in good



Fig. 1. TEM image of the sonochemically prepared (a) Au<sub>2</sub>S<sub>3</sub>, (b) Au.

agreement with the theoretical value of 80.41% for  $Au_2S_3$ . The transmission electron microphotograph (TEM) of the as-prepared  $Au_2S_3$  shows the size and morphology of the product. The particles are flake-like with an average size of about 40 nm and agglomerated into porous clusters, as indicated in Fig. 1a.

Fig. 2 shows the XRD patterns of samples, obtained during ultrasonic irradiation of Au(CH<sub>3</sub>COO)<sub>3</sub> using different irradiation times. After 30 min of irradiation, the sample is almost pure Au(CH<sub>3</sub>COO)<sub>3</sub> with some indicated peaks of gold. After 1 h, the peaks of gold are clearly visible but some unreacted gold acetate can also be observed. The decomposition of  $Au(CH_3COO)_3$  is completed after 3 h of irradiation, yielding pure nanocrystalline gold. By using the Debye-Scherrer equation with the shape factor of 0.95, the average crystallite size of 13 nm has been calculated from the half-width of diffraction peaks. The diffraction patterns of the products, prepared by using irradiation times longer than 3 h, show no significant differences compared to the sample after 3 h. The XRD pattern of metallic gold, obtained by the thermal decomposition of Au(CH<sub>3</sub>COO)<sub>3</sub>, is shown for comparison. The TEM image of the sonochemically prepared gold particles after 3 h irradiation time (Fig. 1b) shows that the particles are mainly spherical with diameters ranging from 10 to 15 nm, which is consistent with XRD results.

As mentioned earlier, the synthesis of  $Au_2S_3has$  been carried out using a cooling bath with a temperature of 0 °C. Controlling the temperature of the cooling bath is very important in the synthesis, since the products, obtained at higher temperatures, always contained some nanocrystalline gold in addition to the synthesized Au<sub>2</sub>S<sub>3</sub>. Although the intense heating (up to 5000 °C), produced upon the acoustic cavitation, is limited to some localized spots in the liquid, the temperature of the bulk liquid also slowly increases during the reaction and can reach up to 75 °C after 3 h of irradiation without cooling. At this temperature, the reaction product is a mixture of Au and Au<sub>2</sub>S<sub>3</sub>. When the reaction vessel was cooled with water at  $15 \pm 1$  °C, there were still some peaks of gold in the XRD pattern of the product, while pure gold(III) sulfide was produced at 0 °C.

While the determination of the exact reaction mechanism has not been a subject of our study, it is obvious that during the irradiation, two processes take place simultaneously: the decomposition of Au(CH<sub>3</sub>COO)<sub>3</sub> and the reaction between the as-formed Au particles and elemental sulfur. Senftle and Wright reported [9] the synthesis of gold sulfides using electrolitically formed short-chain sulfur. Unlike the ordinary  $\alpha$ -sulfur with his S<sub>8</sub> rings, the short-chain sulfur forms chains of indeterminant length with an electron on each terminal sulfur atom and is much more reactive. It can be assumed that a similar process takes place upon sonification of the sulfur solution in decalin, since it is well known that bond breakage can occur due to the extreme conditions during the cavitional collapse.

In summary, amorphous  $Au_2S_3$  and nanocrystalline gold have been successfully prepared using  $Au(CH_3COO)_3$  and S as reagents and decalin as the solvent. The method has proved to be simple and effi-





cient. The use of toxic chemicals, such as  $H_2S$ , or complicated operations-like gas deposition were avoided by using the sonochemical method. We expect that the method may be extended to the preparation of some other nanosized sulfides and selenides.

### References

- [1] X. Peng, J. Wickman, A.P. Alvisatos, J. Am. Chem. Soc. 120 (1998) 5343–5344.
- [2] X. Peng, L. Manna, W. Yang, J. Wickman, E. Scher, A. Kadavanich, A.P. Alvisatos, Nature 404 (2000) 59–61.
- [3] A.P. Batra, A.L. Laskar, L.M. Slifkin, J. Phys. Chem. Solids 30 (1969) 2053.
- [4] R.J. Poddenphatt, in: The Chemistry of Gold, Elsevier, Amsterdam, 1978, p. 39.
- [5] B.F. Johnson, R. Davis, Comprehensive Inorganic Chemistry, Pergamon Press, Oxford, 1973 (Chapter 29).
- [6] H. Hirsch, A. de Cugnac, M. Gadet, J. Pouradier, Cristallographie du sulfure aureux, C.R. Acad. Sci. Paris 263 (1966) 1328.
- [7] U. Antony, A. Lucchesi, Gazz. Chim. Ital. 20 (1890) 61.
- [8] A. Gubtier, E. Durrwachter, Anorg. Allg. Chem. 121 (1922) 266.
- [9] F.E. Senftle, D.B. Wright, Z. Naturforsch. 41b (1986) 1081– 1084.

- [10] Y. Saito, S. Nakahara, B.K. Teo, Inorg. Chim. Acta 148 (1988) 21–24.
- [11] T. Inami, M. Kobiyama, S. Okuda, H. Maeta, H. Ohtsuka, NanoStruct. Mater. 12 (1999) 657–660.
- [12] S. Okuda, M. Kobiyama, T. Inami, S. Takamura, Scripta Mater. 44 (2001) 2009–2012.
- [13] K.S. Suslick, Sci. Am. 56 (1989) 80-86.
- [14] K.S. Suslick, Science 247 (1990) 1439–1445.
- [15] K.S. Suslick, D.A. Hammerton, R.E. Cline Jr., J. Am. Chem. Soc. 108 (1986) 5641–5642.
- [16] K.S. Suslick, S.B. Chloe, A.A. Cichowlas, A.A. Grinstaff, Nature 353 (1991) 414.
- [17] M.W. Grinstaff, M.B. Salamon, K.S. Suslick, Phys. Rev. B 48 (1993) 269.
- [18] R. Bellissent, G. Galli, T. Hyeon, S. Magazu, D. Majolino, P. Migliardo, K.S. Suslick, Phys. Scr. T 57 (1995) 79.
- [19] K.S. Suslick, G.J. Price, Annu. Rev. Mater. Sci. 29 (1999) 295– 326.
- [20] G.Z. Wang, W. Chen, C.H. Liang, Y.W. Wang, G.W. Meng, L.D. Zhang, Inorg. Chem. Commun. 4 (2001) 208–210.
- [21] J.H. Zhan, X.G. Yang, D.W. Wang, Y. Xie, Y.T. Quian, Inorg. Chem. Commun. 2 (1999) 447–449.
- [22] M. Kristl, M. Drofenik, Inorg. Chem. Commun. 6 (2003) 68–70.
- [23] B. Li, Y. Xie, J. Huang, Y. Liu, Y. Qian, Chem. Matter. 12 (2000) 2614–2616.
- [24] B. Li, Y. Xie, Y. Liu, J. Huang, Y. Qian, J. Solid State Chem. 158 (2001) 260–263.