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August 2002

Materials Letters 55 (2002) 253–258

**MATERIALS  
LETTERS**

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# Preparation of copper monosulfide and nickel monosulfide nanoparticles by sonochemical method

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Received 20 August 2001; accepted 24 August 2001

## Abstract

This paper presents a novel method for the preparation of copper monosulfide (CuS) and nickel monosulfide (NiS) nanoparticles via a sonochemical route from an aqueous solution containing metal acetate [Cu(CH<sub>3</sub>COO)<sub>2</sub> or Ni(CH<sub>3</sub>COO)<sub>2</sub>] and thioacetamide (TAA) in the presence of triethanolamine (TEA) as a complexing agent under ambient air. The products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray analysis (EDAX). The as-prepared nanoparticles have regular shape, narrow size distribution and high purity. It is found to be a mild, convenient and efficient method for the preparation of CuS and NiS nanoparticles. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Sonochemistry; Synthesis; Nanomaterials; CuS; NiS

## 1. Introduction

In the past decade, synthesis and physical characterization of nanocrystalline sulfide semiconductors have attracted significant interest and is still the subject of intense investigation owing to their important physical and chemical properties [1–6]. Among these materials, CuS and NiS are two useful semiconductive materials. CuS has been found to be an important material which possesses nearly ideal solar control characteristics [7]. NiS has a number of applications in various fields such as IR detectors, electrode in PEC storage devices, solar storage and hydrosulfurization catalysis [7–9].

Currently, the sonochemical method has been used extensively to generate novel materials with unusual properties since they form particles of a much smaller size and higher surface area than those reported by other methods [10]. The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth and implosive collapse of bubbles in a liquid. The implosive collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubbles. The temperature is estimated to be 5000 K, the pressure reaches over 1800 kPa and the cooling rate is over 10<sup>10</sup> K/s when the bubbles explode [11], which enables many chemical reactions to occur. These extreme conditions attained during bubble collapse have been exploited to prepare various materials including metals [11–14],

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carbides [15], oxides [16–18], selenides [19], tellurides [20] and composite [21–23] nanoparticles.

Ultrasound irradiation offers a very attractive method for the preparation of nanosized materials and has shown very rapid growth in its application to materials science due to its unique reaction effects. The extreme conditions formed during ultrasound irradiation have been applied to prepare some nanophasic sulfides. For example, Mdleleni et al. [24] have sonicated a slurry of molybdenum hexacarbonyl and sulfur in an isodurene solution and obtained MoS<sub>2</sub>. Arul Dhas et al. [25] synthesized ZnS nanoparticles on silica microspheres by sonicating a slurry of silica microspheres, zinc acetate and thioacetamide. Zhu et al. [26] developed a sonochemical route to prepare HgS and PbS nanoparticles in an ethylenediamine solution. The sonochemical preparation of CdS nanoparticles in aqueous solution [27–29] and CS<sub>2</sub>–water–ethylenediamine (CWE) system [30] has also been recently reported. Herein, we applied ultrasound irradiation to synthesize CuS and NiS nanoparticles. Spherical CuS and NiS nanoparticles with narrow size distribution and high purity were prepared by sonicating an aqueous solution containing metal acetates and TAA in the presence of TEA. It is found to be a mild, convenient and efficient method for the preparation of CuS and NiS nanoparticles in only one step.

## 2. Experimental

All the reagents used in our experiments were of analytical purity and were used without further purification. Ni(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O and Cu(CH<sub>3</sub>COO)<sub>2</sub> were purchased from Beijing Chemical Reagents Factory (China). TEA and TAA were purchased from Nanjing Chemical Reagents Factory (China). Absolute ethanol and acetone were purchased from Shanghai Chemical Reagent Factory (China).

In a typical procedure, 0.01 mol M(CH<sub>3</sub>COO)<sub>2</sub>, 0.012 mol TAA and 5 ml TEA were introduced into 100 ml distilled water in a 150-ml round-bottom flask. Then the mixture solution was exposed to high-intensity ultrasound irradiation under ambient air for 50 min. Ultrasound irradiation was accomplished with a high-intensity ultrasonic probe (Xinzhì, China; 0.6 cm diameter; Ti horn, 20 kHz, 60 W/cm<sup>2</sup>) immersed directly in the reaction solution. At the end of the

reactions, a great amount of black precipitates occurred. After cooled to room temperature, the precipitates were centrifuged, washed by distilled water, absolute ethanol and acetone in sequence, and dried in the air at room temperature. The final products were collected for characterizations. The products were characterized by XRD, TEM, XPS and EDAX.

The X-ray powder diffraction (XRD) patterns were recorded on Shimadzu XD-3A X-ray diffractometer (Cu K $\alpha$  radiation,  $\lambda=0.15418$  nm), employing a scanning rate of 4°/min in the  $2\theta$  range from 20° to 65°. The morphology and size were determined by transmission electron microscopy (TEM). The TEM images were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 kV. The samples used for TEM observations were prepared by dispersing some products in ethanol followed by ultrasonic vibration for 30 min, then placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. Further evidence for the purity of CuS and NiS was obtained by XPS and EDAX. The X-ray photoelectron spectra (XPS) were recorded on ESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Mg K $\alpha$  X-ray as the excitation source and choosing C1s (284.6 eV) as the reference line. The EDAX measurements were performed on the PV9100 instrument.

## 3. Results and discussions

The XRD patterns of the products are shown in Fig. 1. All the reflections in Fig. 1a can be indexed to the pure hexagonal phase CuS according to the literature pattern for CuS [31]. The reflection peaks in Fig. 1b are recognized to be the pure orthorhombic phase NiS. This is also in good agreement with the literature pattern [32]. The broadening of the peaks indicates that the particles are small. The average diameter of the as-prepared CuS nanoparticles is estimated to be ca. 13 nm and that of NiS is calculated to be ca. 18 nm according to the Debye–Scherrer formula [33].

The sizes and morphologies of the as-prepared nanoparticles were studied by TEM. The TEM images (Fig. 2) show that both products are consisted of spherical nanoparticles. The size of the CuS particles

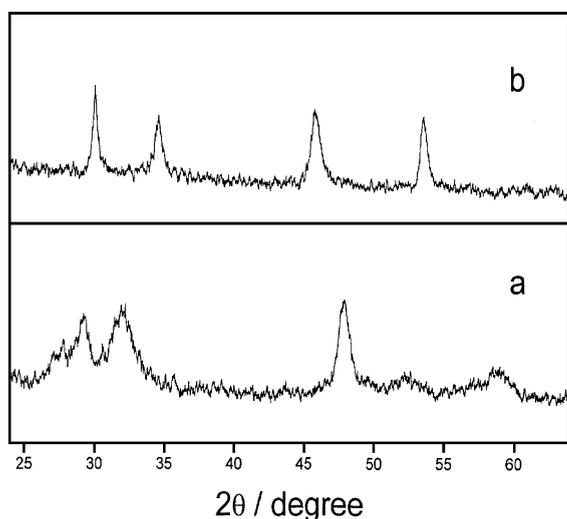


Fig. 1. The powder XRD patterns of the as-prepared nanoparticles: (a) CuS; (b) NiS.

is  $13 \pm 2$  nm and that of NiS particles is  $17 \pm 3$  nm, which are in good accordance with those estimated from the XRD patterns.

The products were characterized by X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray analysis (EDAX) for the evaluation of their composition and purity. No peaks of any impurities such as oxide or metallic copper are detected in the XPS spectra of the as-prepared CuS nanoparticles, indicating the high purity of the product. Fig. 3a and b shows the high-resolution XPS spectra of Cu (2p) and S (2p), respectively. The two strong peaks taken for the Cu region at 932.5 and 952.4 eV are assigned to

the Cu (2p) binding energy. The peaks measured in the S energy region detected at 162.2 and 163.3 eV are attributed to the S (2p) transitions. Peak area of Cu and S cores is measured and quantification of the peaks gives the ratio of Cu:S to be 56.0:44.0, which indicates that the surface of the sample is rich in Cu. XPS primarily monitors concentrations at the surface of the examined samples, which may not be representative of the sample as a whole. The deviation of atomic ratio of Cu:S to the expected 1:1 may be attributed to the excessive  $\text{Cu}^{2+}$  absorbed on the surface of CuS nanoparticles. The as-prepared NiS nanoparticles also have high purity according to the XPS spectra of this sample, and the ratio of Ni to S is calculated to be 58.1:41.9. The EDAX patterns for the products are shown in Fig. 4. Fig. 4a shows the presence of Cu and S peaks. The average atomic ratio of Cu/S is calculated to be 60:40. The EDAX patterns for NiS (Fig. 3b) shows the presence of Ni and S peaks with an average atomic ratio of Ni/S to be 59:41. These results also point out that the surface of the samples is rich in metal due to the absorption of metal ions on the surface of the products which is much larger than that of bulk materials.

The mechanism for the formation of CuS and NiS nanoparticles are probably related to the radical species generated from water molecules by the absorption of the ultrasound energy. Ultrasound wave that is intense enough to produce cavitation can drive chemical reactions such as oxidation, reduction, dissolution and decomposition [10,34]. Other reactions driven by high-intensity ultrasound irradiation such as promotion of polymerization have also been reported. It has

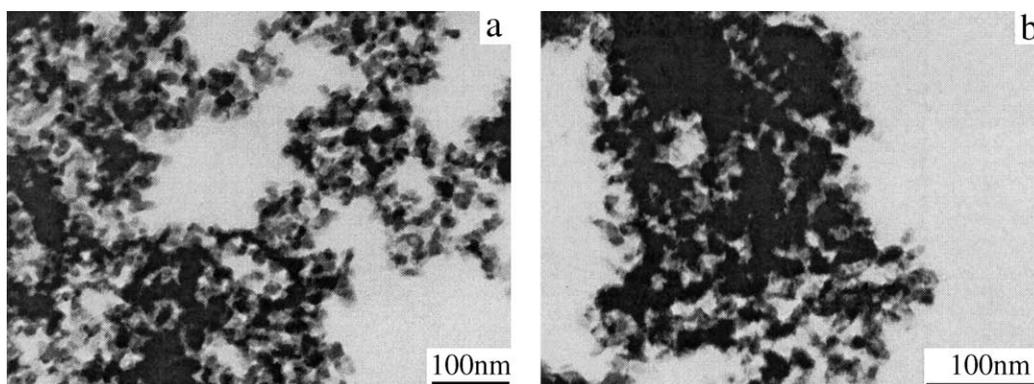


Fig. 2. The TEM images of the as-prepared nanoparticles: (a) CuS; (b) NiS.

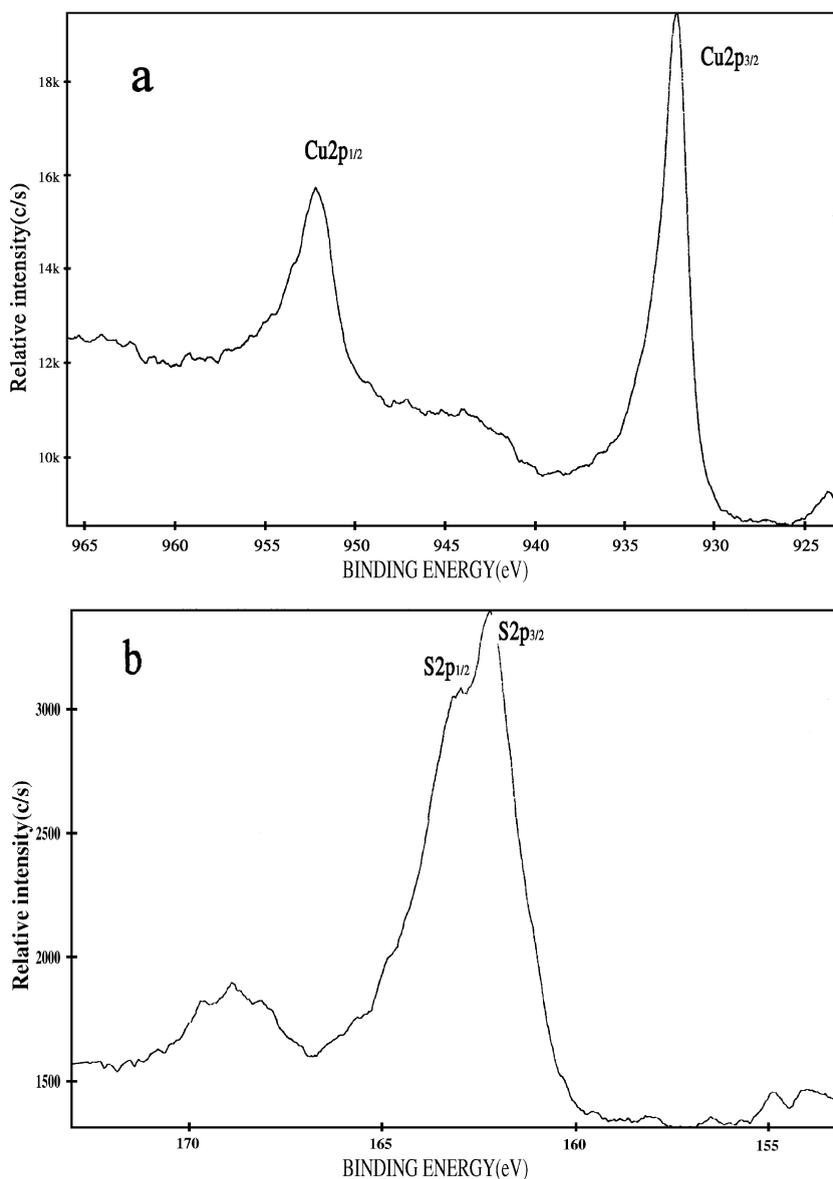


Fig. 3. High-resolution XPS spectra of the as-prepared CuS nanoparticles: (a) Cu 2p; (b) S 2p.

been known that during the sonochemical process, three different regions [34] are formed: (1) the inner environment (gas phase) of the collapsing bubbles, where the elevated temperatures and pressures are produced; (2) the interfacial region between the cavitation bubbles and the bulk solution where the temperature is lower than in the gas-phase region but still high enough to induce a sonochemical reac-

tion; (3) the bulk solution, which is at ambient temperature. Among the three regions mentioned above, it appears that the current sonochemical reaction occurs within the interfacial region, yielding nanoparticles, because of the very high quenching rate experienced by the products. During an aqueous sonochemical process, the elevated temperatures and pressures inside the collapsing bubbles cause water to

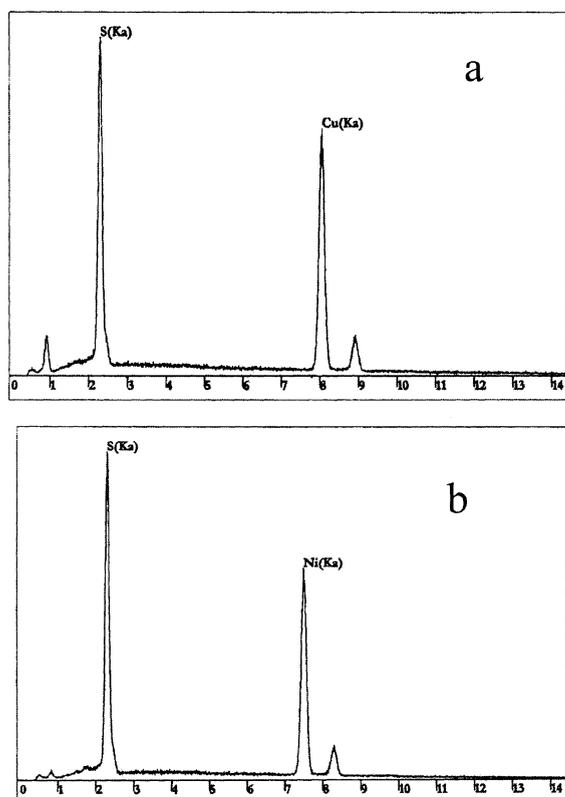
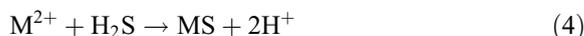
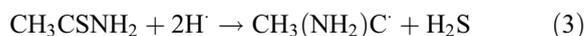
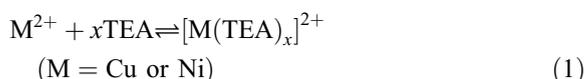


Fig. 4. The EDAX patterns of the as-prepared nanoparticles: (a) CuS; (b) NiS.

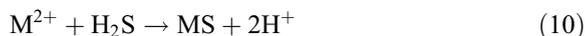
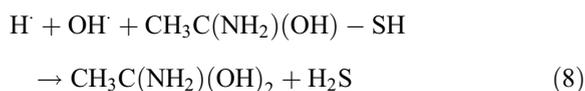
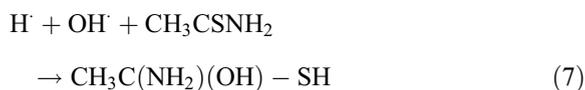
vaporize and further pyrolyze into  $\text{H}^\cdot$  and  $\text{OH}^\cdot$  radicals. The probable reaction process for the sonochemical formation of CuS and NiS nanoparticles in aqueous solution can be summarized as follows:



Firstly, the coordination action between  $\text{M}^{2+}$  and TEA leads to the formation of M–TEA complexes.

Reaction (2) represents the formation of primary radicals by the ultrasound initiated dissociation of water within the collapsing gas bubbles. Reactions (3)–(5) represent the main steps leading to the formation of MS nanoparticles. The in situ generated  $\text{H}^\cdot$  is a highly reducing radical, and can react with TAA rapidly via reaction (2) to form  $\text{H}_2\text{S}$ . Then  $\text{H}_2\text{S}$  reacts with  $\text{M}^{2+}$  ions which are released from the M–TEA complexes to yield MS nuclei. These freshly formed nuclei in the solution are unstable and have the ability to grow into larger MS grains and gets stable finally.

The sonochemical formation of the CuS and NiS may follow another process as well. It can be explained as below. First, the cleavage of water could be linked with the addition across the C=S bond to give  $\text{CH}_3\text{C}(\text{NH}_2)(\text{OH})\text{-SH}$ . Repeating this process would then result in formation of  $\text{CH}_3\text{C}(\text{NH}_2)(\text{OH})_2$  (which would immediately lose water to give  $\text{CH}_3\text{CONH}_2$ ) and  $\text{H}_2\text{S}$ . Then the released  $\text{H}_2\text{S}$  reacts with  $\text{M}^{2+}$  to yield MS.



#### 4. Conclusion

In summary, CuS and NiS nanoparticles have been successfully prepared via a sonochemical route from an aqueous solution containing metal acetate and TAA in the presence of TEA as a complexing agent under ambient air. It is found to be a mild, convenient and efficient method to prepare CuS and NiS nanopar-

articles with regular shape, narrow size distribution and high purity in only one step. The probable mechanism for the sonochemical formation of the CuS and NiS nanoparticles in aqueous solution is discussed in this paper.

### Acknowledgements

This work is supported by the National Natural Science Foundation of China (NSFC, no. 50072006). Financial supports from the Foundation of Ministry of Education for returnee, Jiangsu New technology program, China (no. BG2001039) and Analytical Foundation of Nanjing University are also gratefully acknowledged.

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