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Materials Letters 59 (2005) 529–534

materials letters

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# Characterization of silver sulfide nanoparticles synthesized by a simple precipitation method

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Received 16 June 2004; received in revised form 6 October 2004; accepted 20 October 2004
Available online 30 October 2004

**Abstract**

Silver sulfide nanoparticles with different sizes were synthesized using a simple aqueous precipitation. Particles were obtained in the presence of three stabilizing agents controlling thus particle size and agglomeration. The particles obtained were characterized using XRD, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal and spectroscopy techniques. We observed a "size quantization" effect reflected in a shift on the band gap value of smaller sample obtained.


*Keywords:* Nanomaterials; Semiconductors

## 1. Introduction

Semiconductor nanoparticles have been investigated over the past years due to their potential applications in microelectronics and due to their specific optic, electronic and catalytic properties. Methods to prepare semiconductor nanoestructures can be classified into physical methods and chemical methods. Physical methods use molecular beam and lithography techniques obtaining well defined nanostructures which are used in high precision electronic and magnetic measurements [1]. Among many chemical routes to synthesize semiconductor nanoparticles [2], the colloidal one represents an option due to their versatility and their relative facility; using this technique, one can obtain almost any material choosing adequate reactants and controlling the reaction parameters. Silver sulfide can be used as giant magnetoresistor (GMR) [3]; silver sulfide thin films with a silver excess can be used as detectors in the infrared region [4] and silver sulfide clusters are used in photographic sensibility [5]. There are many and different methods to synthesize silver sulfide nanoparticles, some can give silver sulfide particles with cube [6] or dendrite forms [7]; silver sulfide particles that are bioactive can also be obtained [8,9], silver sulfide nanoparticles under 15 nm in size were synthesized [10–12] and recently, simpler methods are appearing [13]. Each method has advantages and produces particles with particular properties. In this work, silver sulfide nanoparticles were synthesized using a simple aqueous precipitation. Three stabilizing agents were used in order to prevent particle growth and agglomeration: Triton X-100, a very well-known surfactant with an hydroxyl functional group; mercaptoacetic acid and 3-mercapto-1,2-propanediol, both containing a thiol functional group. We used these agents to probe that the functional group plays an important role in the prevention of particle growth and agglomeration.

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doi:10.1016/j.matlet.2004.10.043

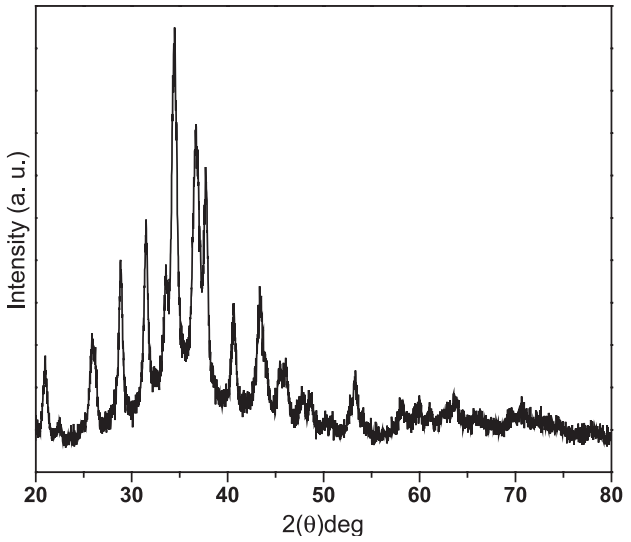


Fig. 1. X-ray diffraction pattern of the sample synthesized using 3-mercapto-1,2-propanediol as stabilizing agent.

Also, we determined the optical band gap using the simple diffuse reflectance spectroscopy.

## 2. Experimental section

### 2.1. Synthesis

Silver nitrate was dissolved in 1 L of deionized water to a concentration of 8 mM. This solution was placed in a 2-L reaction vessel. Under stirring (200 rpm) 10 mmol of Triton X-100, 3-mercapto-1,2-propanediol or mercaptoacetic acid was added and the mixture was stirred for an additional 5 min. Ammonium sulfide (4 mmol) dissolved in 100 mL of deionized water was added dropwise under ambient conditions. When using 3-mercapto-1,2-propanediol or mercaptoacetic acid as protective reagents, this method yields dispersions that are stable even during months. For comparison purposes, an additional sample was obtained following the same route but using no stabilizing agent.

Hereafter, the particles prepared without stabilizing agent will be referred as $Ag_2S$, silver sulfide powders prepared in the presence of Triton X-100 as $Ag_2S$-T; in the presence of mercaptoacetic acid as $Ag_2S$-M and those obtained in presence of 3-mercapto-1,2-propanediol as $Ag_2S$-P.

### 2.2. Characterization

When applicable, SEM characterization was carried out using the stable dispersions. XRD, thermal and spectroscopic analyses were made using the dried powders obtained by precipitation by means of ionic strength adjustment. X-ray diffraction patterns were recorded with a Rigaku 2200 powder X-ray diffractometer. The nickel filtered Cu Kα ($\lambda$=1.5418 Å) radiation was used at 36 kV and 30 mA. Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer TGA 7, using nitrogen as purging gas, at a scanning rate of 10 °C/min. Differential thermal analysis (DTA) was obtained on a Perkin Elmer instrument model DTA 7 using nitrogen as purging gas, also at a scanning rate of 10 °C/min. The morphology was observed by scanning (SEM) and transmission electron microscopy (TEM). SEM images were obtained using a XL-30 scanning electron microscope (Philips, Netherlands). EDS measurements (energy-dispersive X-ray spectrometry) were carried out using an X-ray microanalyzer (DX-4I, EDAX) built on the scanning electron microscope. TEM images were obtained using a JEOL JEM 2000 FXII using an accelerating voltage of 200 kV. Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid. Optical analysis was made in an Oceanoptics S2000 and NIR spectra were obtained using an NIR Ocean Optics system.

## 3. Results and discussion

Fig. 1 shows the diffraction pattern of the sample $Ag_2S$-P. All patterns obtained agree with the published data (JCPDS 14-072). The difference between the diffraction patterns of the different samples is only the peak broadening due to the particle size. The nanoparticles synthesized are in the monoclinic form which is the stable form of silver sulfide at room temperature. Average particle size was calculated using Scherrer's equation and the results are reported in Table 1. Differences in particle agglomeration were observed by SEM. The samples named $Ag_2S$ and $Ag_2S$-T show strong agglomeration (Fig. 2a and b). In Fig. 3, a closer view of these samples is presented, and we can see that they are formed by nanometrical particles; the observed particle size in these samples is not consistent with those presented in Table 1 probably due to a different size distribution in both samples, the average particle size obtained by analysis made by X-ray diffraction is considered over a large amount of particles, which is very difficult to do in SEM analysis, particle size observed in Fig. 3 represents a very small fraction of the sample. The particles named $Ag_2S$-M and $Ag_2S$-P are loose agglomerated (Fig. 2c and d).

Particle morphology was observed using TEM. Images of sample $Ag_2S$-M are presented in Fig. 4, the particles present ellipsoidal and spherical morphology and their sizes are between 20 and 50 nm.

Table 1
Average particle size calculated using Scherrer's equation

| Synthesis conditions | | | |
|---|---|---|---|
| Sample | pH | Stabilizing agent | Particle size (nm) |
| $Ag_2S$ | 7 | Without stabilizing agent | 64.6 |
| $Ag_2S$-T | 7.5 | Triton X-100 | 74 |
| $Ag_2S$-M | 1.9 | Mercaptoacetic acid | 52 |
| $Ag_2S$-P | 2 | 3-mercapto-1,2-propanediol | 30.8 |