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## Structural and spectroscopic characterization of prepared Ag<sub>2</sub>S nanoparticles with a novel sulfuring agent



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#### HIGHLIGHTS

- Silver sulfide nanostructures were synthesized by solvothermal method.
- Shape of obtained sample was controlled by reaction conditions.
- 2-(Benzylidene amino) benzenethiol was chosen as a the newest sulfuring agent.
- Effects of different parameters on purity, size and morphology were investigated.

## GRAPHICAL ABSTRACT



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## Introduction

Transition metal chalcogenides such as sulfides, selenides and tellurides are usually found in minerals. They have attracted world-wide attention owing to the interesting properties, in recent decades [1]. They have commercial applications in pigments, semiconductors, fluorescence devices and even superconductors [2,3]. Silver sulfide is an important chalcogenide due to its photoelectric and thermoelectric properties, which has been world-wide appli-

## ABSTRACT

Ag<sub>2</sub>S nanoparticles were prepared by a solvothermal process via reaction of Ag(NO<sub>3</sub>) and a new sulfuring agent from class of thio Schiff-base (2-(benzylidene amino) benzenethiol (C13H11NS)) in presence of various solvents. Spectra such as X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SEAD), ultraviolet-visible (UV-Vis) spectroscopy, thermo gravimetric-differential thermal analysis (TG-DTA), and Fourier transform Infrared (FT-IR) employed to characterize the synthesized products. Results of this paper indicate that shape and size of the silver sulfide can be controlled by means of setting certain reaction parameters such as the reaction temperature, presence of surfactant, and type of solvent. Silver sulfide nanoparticles with different morphology and size successfully prepared. In addition, the growth mechanisms of the Ag<sub>2</sub>S nanoparticles discussed preliminarily.

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cations in various fields of science and technology such as, photo conducting cells, photovoltaic cells, IR detectors [4] and electrochemical storage cells [5,6]. It is also well recognized as a mixed ionic and electronic conductor at high temperatures above 200 °C. Various techniques has been suggested for synthesis and properties characterization of silver sulfide such as chemical bath deposition (CBD) [8,9], spray pyrolysis deposition (SPD) [10], successive ionic layer adsorption and reaction (SILAR) [11], molecular beam epitaxy (MBE) [12], gamma irradiation [13], thermal evaporation [14] and sol-gel and ion implantation techniques [15], Among different methods of preparation, liquid-based techniques as well as gas phase-based techniques, are aiming highly

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crystalline particles with almost monodisperse size distribution and regular morphology [16–20]. The polyol route applied herein provides a promising preparative approach to such sulfide particles. The polyol method was early part used for the preparation of elemental metals and alloys [21-24], because alcohols (e.g. glycerol, glycol) with high boiling provide a suitable metal precursor for preparation metal sulfide, alloys and elemental metals. Recently metal oxide particles have been prepared with this route [25,26]. Generally, reaction of the formation of binary chalcogenides is relatively slow in polyol methode; till now, the synthetic strategies based on the polyol route to binary chalcogenides are used under microwave irradiation [27]. Yang's group also developed solvothermal route in polyol solvent to sulfides using autoclave as pressure equipment [28]. In our present investigations, the polvol method was found to be suitable for the synthesis of a host of binary metal sulfides under moderate conditions.

### Experimental

#### Reagent

All reagents and solvents were of analytical grade and were used as received without further purification.

#### Synthesis of Ag<sub>2</sub>S nanocrystals

In a typical experiment, two solutions were prepared, respectively. (A) The 0.63 ml benzaldehyde was dissolved in propylene glycol (10 ml) under stirring. In a separate beaker, 0.63 ml (5.88  $\times$  10<sup>-3</sup> mol) 2-aminothiophenol was dissolved in 10 ml absolute propyleneglycol and added drop wise to previous solution under 30 min stirring at room temperature (the molar ratio of 2-ATP and benzaldehyde is 1:1). (B) 0.5 g  $(2.9 \times 10^{-3} \text{ mol})$ of Ag(NO<sub>3</sub>) was dissolved in 50 ml propylene glycol under magnetic stirring(the molar ratio of Ag(NO<sub>3</sub>) and ligand is 1:2); solution A was added into solution B slowly under magnetic stirring for 2 h finally the color of mixture becomes vellow. The final solution was transferred to a 70 ml Teflon-line stainless steel autoclave and filled with propylene glycol up to 80% of the total volume. The autoclave was sealed and maintained at 160 °C for 12 h. After thermal treatment, the autoclave was cooled to room temperature and the resulting black precipitate was collected, filtered, and washed with distilled water and absolute ethanol for several times to remove the unreacted chemicals, and finally dried in vacuum oven at 70 °C for 6 h.

#### Characterization

X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Ka radiation. The compositional analysis was done by energy dispersive X-ray (EDX, Kevex, Delta Class I), scanning electron microscopy (SEM) images were obtained on LEO. Transmission electron microscopy (TEM) images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage ao 100 kV Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of samples were taken on a JASCO, (190–2700 nm), UV–Visible scanning spectrometer (Model V-670). Thermogravimetric–differential thermal analysis (TG–DTA) were carried out using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 mL min<sup>-1</sup> and a heating rate of 10 °C min<sup>-1</sup>.

#### **Results and discussion**

Synthesis of Ag<sub>2</sub>S at temperature of 160 °C for 12 h with propylene glycol as solvent has been selected as a basic reaction in this work and systematic reaction conditions such as reaction temperature, using of surfactant and solvent type on the morphology and size of the products has been investigated.

The crystal structure and composition of the as-prepared products were determined by XRD. The XRD patterns of the Ag(NO<sub>3</sub>) and thio Schiff-base (2-(benzylidene amino) benzenethiol (C13H11NS)) obtained in absence of surfactant, presence of surfactants (sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB) and PEG 20,000), in H<sub>2</sub>O and 1-butanol solvents have been shown in Fig. 1a-f, respectively. Peak in Fig. 1a; correspond to the reflections of Ag<sub>2</sub>S. These patterns are indexed as cubic phase and orthorhombic phase which are very close to the literature values (JCPDS No. 02-0998 and 03-0844 respectively). The crystallite size measurements were also carried out using the Scherrer equation,  $Dc = K \lambda / \beta cos \theta$ . Where, K is about 0.9,  $\beta$  is the breadth of the observed diffraction line at its half intensity maximum and  $\lambda$  is the wavelength of X-ray source used in XRD. The estimated crystallite size of sample is 47.04 nm. The purity of the nanoparticles was also reckoned up by energy-dispersive X-ray spectroscopy. When surfactants are used in the reaction, mercuric has been synthesized instead of mercuric sulfide. Indeed, surfactants acted as reducer. Fig. 1b-d patterns are indexed as cubic phase which are very close to the literature values (JCPDS No. 87-0597). The X-ray diffraction (XRD) patterns of the prepared Ag<sub>2</sub>S nanoparticles in H<sub>2</sub>O and 1-butanol solvents are shown in Fig. 1e and f, all the characteristic peaks can be well-indexed as monoclinic phase which are very close to the literature values (JCPDS No. 65-2356).

Novelty of this study compared to other research carried out this is which for synthesize of silver sulfide was used from a new sulfuring agent from class of thio Schiff-base, without any surfactant and reduce agent in diverse solvents. Experimental results in this paper



Fig. 1. XRD patterns (a)  $Ag_2S$  spherical nanoparticles in absence of surfactant, (b) in presence of SDS, (c) CTAB, (d) PEG 20,000, (e)  $H_2O$  as solvent and (f) 1-butanol as solvent.

indicate that presence of surfactant and type of solvent are effective on the size regularity of particles, thio Schiff-base ligand playing both complexing agent role and sulfuring agent role. Herein, the possible process could be explained in the following step: First, thio Schiff-base (2-(benzylidene-amino)-benzenthiol) was prepared with benzaldehyde and 2-aminothiophenol, in the second step, metal salt was dissolved in propylene glycol and interaction occurs between solvent OH groups and Ag<sup>+</sup>. when the former solution was dropped into the latter solution under stirring, interaction occurs between ligand N and S groups with Ag<sup>+</sup> and upon heating a reaction medium up to a sufficiently high temperature, the precursors chemically transform into active atomic or molecular species, forming nanocrystals whose subsequent growth is greatly affected by the presence of ligand and solvent molecules, which can prevent particle further growth and aggregation. Given this probable mechanism, thio Schiff-base ligand in hydrothermal system completely has been destructed and finally was produced Ag<sub>2</sub>S without any possible impurity phases such as remaining of thio Schiff-base and S because The strong and sharp reflection peaks in the XRD pattern confirms pure Ag<sub>2</sub>S nanocrystals. In addition, in the next sections we will see energy-dispersive X-ray analysis (EDX) and Fourier transform infrared FT-IR spectrums imprinted seal of approval on the purity produced Ag<sub>2</sub>S nanoparticles.

EDAX analysis of Ag<sub>2</sub>S nanoparticles is illustrated in Fig. 2. The lines of Ag and S are obviously observed. In addition, neither N nor C signals were detected in the EDAX spectrum, which means there exist no possible impurity phases such as organic sulfur source or propylene glycol in spherical Ag<sub>2</sub>S nanoparticles. FT-IR of the complex of Ag(NO<sub>3</sub>) with ligand synthesized and Ag<sub>2</sub>S nanoparticles prepared at temperature of 160 °C for 12 h in hydrothermal method with solvent of propylene glycol are shown in Fig. 3(a) and (b) respectively. Absorptions of 3442, 1569, 739, 611 and 477 cm<sup>-1</sup> in Fig 3(a) related to O—H, C=N, C—S, Ag—N and Ag—S bands respectively and weak absorption appeared in 1631.78 cm<sup>-1</sup> in spectrum of Ag<sub>2</sub>S attributed to the presence of a small amount of sulfur-containing ligands adsorbed on the surface of Ag<sub>2</sub>S, an absorption at 3441.32 cm<sup>-1</sup> is related to stretching vibrations of O—H bond.

SEM images of Ag<sub>2</sub>S obtained at different temperatures of 140 °C, 160 °C, 180 °C and 200 °C are illustrated in Fig. 4a–d respectively. At temperatures of 140 °C with mole ratio Ag/sulfur sources 1:2, mixture of spherical and cubic nanoparticles are synthesized. With increasing temperature to 160 °C smaller spherical nanoparticles are achieved. While at temperature of 180 °C and 200 °C, smaller nanoparticles with respect to the previous one are noticeable. But particles are more disciplined in temperature 160 °C. The results confirm that in four different circumstances, nanoparticles with average size of less than 100 nm were obtained.

For investigating the effect of surfactant on the morphology and size of the products, the reaction carried out in presence common surfactants such as anionic (sodium dodecyl sulfate (SDS)), cationic (cetyltrimethyl ammonium bromide (CTAB)) and polymeric (PEG



Fig. 2. EDAX spectra of Ag<sub>2</sub>S spherical nanoparticles.

20,000) which they are illustrated in Fig. 5a–c, respectively. SEM images of as product Ag in presence of SDS are shown in Fig. 5a; sodium dodecyl sulfate (SDS) as an anionic surfactant can self aggregate into cubic, hexagonal and lamellar structures [29,30]. In this paper, we used this unique SDS cubic structure. For anionic surfactants it seems SDS capped  $Ag^{2+}$  and with this approach limited the formation of  $Ag_2S$  and it will lead to reduction of  $Ag_2S$  to Ag. Also SDS, as an anionic surfactant, has different influence on the morphology. Due to its amphiphilic nature, it forms stable micelles in solvent in which spherical nanostructures form easily [31].

CTAB as a cationic surfactant was occupied to investigate the influence of cationic active groups on morphology of the products. Due to its cationic head group, CTAB easily interact with free sulfur groups on the surface of nanoparticles and covered them, with this approach limited the formation of Ag<sub>2</sub>S and it will lead to reduction of Ag<sub>2</sub>S to Ag.

Fig. 5b shows SEM image of the Ag sample prepared in presence of CTAB. It can be clearly observed that CTAB has changed the morphology The SEM image (Fig. 5c) shows that nanospheres are also formed in presence of PEG 20,000 because this polymer attaches to the particle surface through its active oxygen groups. This interaction can be result to the reduction of silver ions. Due to PEG 20,000 special structure, it covers Ag naoparticles in which separate and small spherical nanoparticles form easily. Scheme 1. shows probably the mechanism for the preparation of different morphologies of Ag in different surfactants schematically.

SEM images of Ag<sub>2</sub>S nanoparticles that synthesized in H<sub>2</sub>O, 1-butanol, propylene glycol and ethylenediamine as solvent are illustrated in Fig. 6(a-d), respectively. Results shows in H<sub>2</sub>O solvent bulk products are obtained and in 1-butanol solvent nanostructure products with size of lesser 100 nm are observed. We speculate that polyols and alcohols with diverse position and number of OH group play an important role in determining the geometric structures and morphologies of the final products. Propylene glycol has hydroxyl groups with more than 1-butanol and H<sub>2</sub>O, it can



Fig. 3. FT-IR spectra (a) the complex of  $Ag(NO_3)$  with ligand synthesized and (b)  $Ag_2S$  spherical nanoparticles.



Fig. 4. SEM images of the Ag<sub>2</sub>S nanostructure prepared in propylene glycol solvent for 12 h at (a) 140 °C, (b) 160 °C, (c) 180 °C and (d) 200 °C.

provide spherical nanoparticles with a more uniform and regular than alcohol solvent. It has been reported that the hydroxyl groups of polyol can coordinate with Ag<sup>2+</sup> to form complexes [32] and provide affect selective growth for Ag<sub>2</sub>S but in H<sub>2</sub>O solvent due to the lack of interaction between water and cations, amorphous and large nanoparticles are formed. Plus, in hydrothermal system the dielectric constant and viscosity are also important [33,34]. Fig. 6d shows as-synthesized Ag<sub>2</sub>S nanoparticles in ethylenediamin as solvent. Ethylenediamin is a strong bidenate ligand, which it might act as a coordinating alkali solution. So, products are formed with morphologies of nanorod and nanoparticles. That is why, ethylenediamin is considered as a vital factor in the growth of nanoparticles in such as solvothermal process [35–37]. In addition, the dielectric constant, viscosity of solvent and the increased temperature within a hydrothermal medium have a significant effect on the speciation, solubility, and transport of solids. When dielectric constant is a low in a solvent, the ions saturation easily forms to result in high Ag<sub>2</sub>S monomer concentration, which is a crucial precondition for non-equilibrium crystal growth and provided formless silver sulfide nanoparticles. Also, water by having high



Fig. 5. SEM images of the Ag<sub>2</sub>S nanostructure at 160C for 12 h in propylene glycol solvent with (a) SDS, (b) CTAB, (c) PEG 20,000.



Scheme 1. Schematic the effect of surfactants on the morphology of Ag.



Fig. 6. SEM images of the Ag<sub>2</sub>S nanostructure prepared at 160 °C for 12 h in (a) H<sub>2</sub>O, (b) 1-butanol (c) propylene glycol and (d) ethylenediamin.

the dielectric constants provided spherical which are separate from each other as compared to propylen glycol solvent. At room temperature, the dielectric constants of the four solvents can be compared as follows:  $H_2O$  (80.1) > propylen glycol (32.1) > 1-butanol (17.51) > en (14.2) [38]. Obviously, propylene glycol is the best solvent of them for selective anisotropic growth of silver sulfide, because its most balance dielectric property makes it possible to prepare an appropriate  $Ag_2S$  monomer concentration for preferential growth. Scheme 2 is illustrating the formation of  $Ag_2S$  samples at various conditions.

As previously mentioned privilege of this work is application of a new thio Schiff-base as sulfur and capping agent for synthesizing of silver sulfide nanoparticles. Thio Schiff-base synthesized with high steric hindrance is a suitable capping agent for preparation of nanoparticles. Schiff-base group causes nucleation to be occurred rather than the growth.

The optical absorption spectrum of  $Ag_2S$  nanoparticles is represented in Fig. 7a it demonstrates absorption peaks at 320 nm, which according Fig. 7b the band gap energy of  $Ag_2S$  synthesized are 3.1 eV. (The band gap energy of bulk  $Ag_2S$  is 1.1 eV) which this blue shift is attributed to decrease in the particle size which cause to change in particle energy levels and finely increase the band gap and blue shift occurrence.

The size and morphology of as-synthesized silver sulfide nanoparticles were assessed with transmission electron microscopy (TEM) and selected area diffraction (SAED) pattern measurements.



Scheme 2. Schematic diagram illustrating the formation of Ag<sub>2</sub>S samples at various conditions.



Fig. 7. (a) UV-vis absorption spectra of the prepared Ag<sub>2</sub>S at 160 °C for 12 h in PG and (b) plot to determine the direct band gap of Ag<sub>2</sub>S.

The typical TEM (Fig. 8a–c) and SAED images (Fig. 8e) of the Ag<sub>2</sub>S nanoparticles are shown. The TEM image of the Ag<sub>2</sub>S shows that the particles have cubic crystalline phase but strongly overlapped together and also the particles with an average diameter of 42 nm are shown. SAED pattern of sample is shown in Fig. 8e. Which indicates several sharp rings from (101), (111), (120), (200) plans of Ag<sub>2</sub>S nanoparticles and this pattern confirms that silver sulfide nanoparticles are of polycrystalline with high crystallinity. For further approval the structural aspects, the nanoparticles were examined by HR-TEM. As can be seen from a representative HRTEM image, recorded from edge one of Ag<sub>2</sub>S particle in Fig. 8d. The good lattice fringes show that these nanoparticles are single

crystalline and illustrate the correspondence between the crystallite morphology and the crystal orientation [39]. The HRTEM image shows sharp lattice margins with 0.26 nm spacing, corresponding to the (121) planes. Therefore, the HRTEM image further verifies cubic phase nature of the as-synthesized Ag<sub>2</sub>S nanoparticles and finely there are several cubic silver sulfides overlapped together and created spherical nanoparticles that shows SEM image them.

Thermogravimetry (TG) of  $Ag_2S$  nanoparticles has been represented in Fig. 9. The TG curve illustrates that  $Ag_2S$  undergoes two weight loss steps. When the temperature was lower than 200 °C, the step mainly corresponded desorption of water. The



Fig. 8. (a)-(c) TEM, (d) HR-TEM image and (e) SAED images of the as-synthesized Ag<sub>2</sub>S nanoparticles using the thio Schiff-base at 160 °C for 12 h.



**Fig. 9.** TGA of silver sulfide nanoparticles obtained after removal of the liquid crystal phase by washing with ethanol.

decomposition of the organic template occurred at the temperature range 425–540 °C. After the sample was heated over 540 °C, the sample weight did not change anymore. This samples that only a small amount of the thio Schiff-base molecules was bound to the Ag<sub>2</sub>S nanoparticles after they were washed. Combining the results of the FT-IR spectra, it was obvious that thio Schiff-base ligand molecule still existed in the as-prepared product.

The reported researches have been mostly focused on the inorganic sulfides as sulfur sources. To the best of our knowledge, there is no report on the fabrication of silver sulfide only with presence thio Schiff-base ligand containing 2-aminothiophenol (2-ATP) and benzaldehyde. In comparison to other similar works that illustrated in Table 1, our method is more simple and profitable. In this work, we developed a solvothermal method to synthesize silver sulfide in propylene glycol solvent at 160 °C for only 12 h with difference size. Also the advantage use of this solvent can be expressed such that, polyols with diverse position and number of OH group play an important role in determining the geometric structures and morphologies of the final products. It may be due to the specific interaction between OH groups and Ag<sup>+</sup> ions, which affect selective growth of various layers of lead sulfide. We used surfactant to improve the stability of the suspension against flocculation. Surfactant makes important roles in growth of nanocrystals to different shapes during the solvothermal process. We applied various surfactants, solvent, reaction temperature and compared them with each other.

Therefore, privilege of this work is application of a thio Schiffbase as both complexing and sulfuring agent in an environmentally friendly solvent for synthesizing of silver sulfide nanoparticles. Also can be said which thio Schiff-base and propylene glycol have played a unique role in determination of morphology and size of nanoparticles.

#### Conclusions

Ag<sub>2</sub>S nanoparticles have been prepared using hydrothermal method in a new solvent with a novel sulfur source. For the first time in this study has been used from thio Schiff-base as organic sulfur source and capping agent for prepare of Ag<sub>2</sub>S. In work, the influence of different surfactants such as CTAB (cationic), SDS (anionic), PEG 20,000 (polymeric), reaction temperature and solvent type on the morphology of silver sulfide has been investigated. Results show that by using surfactant of PEG 20,000 at presence propylene glycol solvent particles size were be very smaller than basic reaction because OH groups play an important role in determining the geometric structures, particles size and morphologies of the final products. It may be due to the specific interaction between OH groups and Ag<sup>+</sup> ions, which affect selective growth of various directions of silver sulfide nanocrystals.

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#### Table 1

Characterization comparison of Ag<sub>2</sub>S nanoparticles with other similar works.

Method	Precursors	Size	Morphology	Ref.
Synthesize at ambient temperature	AgNO <sub>3</sub> , S powder, en, PVP	100-120 nm	Hexagonal	[40]
Sonochemical	AgNO3, TGA	100–200 nm	Nanowire	[41]
Synthesize at ambient temperature	AgNO <sub>3</sub> , Na <sub>2</sub> S	12 nm, 120 nm	Nanochain nanoparticle	[42]
Synthesize at ambient temperature	AgNO <sub>3</sub> , Tu, CTAB	80 nm 150 nm	Nanoparticle nanocube	[43]
Emulsion	AgNO <sub>3</sub> , TAA	50 nm	nanorod	[44]
Solvothermal	AgNO <sub>3</sub> , S powder	>20 nm	nanowire	[45]
Hydrothermal	AgNO <sub>3</sub> , Tu	>100 nm	Nanoparticle	[46]
Synthesize at ambient temperature	AgNO <sub>3</sub> , $(C_2H_5)NCS_2$	364 nm	Nanoparticle	[47]

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