Synthesis and Characterization of (Ag$_2$S)$_x$(ZnS) Heteronanostructures

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Abstract. (Ag$_2$S)$_x$(ZnS) heteronanostructures were synthesized by two-stage chemical co-deposition of silver and zinc sulfides using aqueous solutions of zinc nitrate, silver nitrate, sodium sulfide, trisodium citrate and Trilon B. Prepared heteronanostructures were characterized for phase composition and nanoparticles size using X-ray diffraction and the high-resolution transmission electron microscopy. The size of Ag$_2$S nanoparticles in the obtained heteronanostructures depends on the ratios of reagent concentrations and ranges from 9 to 30 nm, the size of ZnS nanoparticles is equal to 4-5 nm.

1. Introduction

Nanostructured semiconductor sulfides are a new class of materials, having dimensions in the 2-30 nm range, which provide one of the greatest potentials for improving performance and extended capabilities of products in a number of industrial sectors especially in electronics. Semiconductor silver sulfide Ag$_2$S and zinc sulfide ZnS are widely used as materials for modern electronics devices. The development of semiconductor nanocomposites consisting of Ag$_2$S and ZnS nanoparticles allows adjusting the band gap of such heteronanostructures.

Production of heteronanostructures based on Ag$_2$S and ZnS allows one to improve laser optics devices, expand the spectral sensitivity of semiconductors to the visible long-wavelength region, and to obtain new nanomaterials for direct conversion of solar energy into electricity, for solid-state ultraviolet (UV) lasers, beta-voltaics and high-speed resistance switches [1-6]. In [7], matchstick-shaped Ag$_2$S-ZnS heteronanostructures were synthesized. These heteronanostructures in the form of ZnS quantum rods with Ag$_2$S quantum dots on the top of the rod were obtained by thermal co-decomposition of such single-source precursors as silver diethyldithiocarbamate Ag$_2$S$_2$CN(C$_2$H$_5$)$_2$ and zinc diethyldithiocarbamate Zn[S$_2$CN(C$_2$H$_5$)$_2$]. The matchstick-shaped Ag$_2$S-ZnS heteronanostructures have been shown to display photoluminescence in both UV/blue and near-infrared (NIR) regions. It is known that doping of zinc sulfide by silver sulfide leads to a large decrease in the band gap. For example, an increase in the Ag$_2$S content in ZnS-Ag$_2$S heteronanostructures up to 10 mol.% is accompanied by an appreciable decrease in the optical band gap $E_g$ from $\sim$3.6 to $\sim$2.1 eV, and also by an increase in the intensity of the absorption band in the infrared region [1]. Thus, change of the content of silver sulfide in heteronanostructures allows one to change the band gap and control optical properties in a wide range.
However, the problem of simple synthesizing heteronanostructures based on nanostructured zinc and silver sulfides has not been solved yet.

In the present work, a study of chemical deposition of \((\text{Ag}_2\text{S})_x(\text{ZnS})\) heteronanostructures is carried out for the first time. A simple method for synthesizing the heteronanostructures based on zinc sulfide doped with silver sulfide is proposed.

2. Materials and Methods

Trisodium citrate, Trilon B and sodium sulfide \(\text{Na}_2\text{S}\) from Sigma Aldrich, zinc nitrate and silver nitrate from domestic market were used. All of the chemicals were of analytical grade (A.C.S) and used without further purification. Aqueous solutions of reagents for synthesis of heteronanostructures based on \(\text{Ag}_2\text{S}\) and \(\text{ZnS}\) sulfides were prepared with the use of high-purity deionized water as a solvent. High-purity deionized water was produced using the Milli-Q Reference (Merck, Millipore) water preparation system. The specific resistivity of water is equal 18.2 M\(\Omega\)-cm at 298 K (electrical conductivity is below 5.5\(\times\)10\(^{-6}\) S\(\cdot\)m\(^{-1}\)), the total content of organic carbon did not exceed 5-10 ppb (5-10 \(\mu\)g\(\cdot\)L\(^{-1}\)).

The solubility products \(K_{sp}\) of sulfides \(\text{ZnS} \quad (K_{sp} = 2.5\cdot10^{-22})\) and \(\text{Ag}_2\text{S} \quad (K_{sp} = 6.3\cdot10^{-50})\) [8] differ very strongly. Therefore, \((\text{Ag}_2\text{S})_x(\text{ZnS})\) heteronanostructures have been synthesized in two stages. First, silver sulfide \(\text{Ag}_2\text{S}\) was synthesized by chemical deposition from aqueous solutions of silver nitrate \(\text{AgNO}_3\) and sodium sulfide \(\text{Na}_2\text{S}\) in the presence of sodium citrate \(\text{Na}_3\text{Cit}\). To obtain colloidal solutions of silver sulfide without \(\text{Ag}\) impurities and without a citrate shell, reaction mixtures with a small relative excess of sodium sulfide \(\text{Na}_2\text{S}\) and a minimum concentration of \(\text{Na}_3\text{Cit}\) were used. The synthesis of a colloidal \(\text{Ag}_2\text{S}\) solution was carried out in the dark in a neutral medium at \(pH \approx 7\). Next, Trilon B was added to an aqueous zinc nitrate solution under continuous stirring. Then, the solution prepared was mixed simultaneously with a sodium sulfide solution and synthesized colloidal silver sulfide solution. The use of Trilon B promoted the formation of nanostructured zinc sulfide on a surface of silver sulfide particles, to occurrence of \(\text{ZnS}\) thin lamelliform nanoparticles, and to formation of \((\text{Ag}_2\text{S})_x(\text{ZnS})\) heteronanostructures at a final stage of synthesis. The compositions of reaction mixtures are given in Table 1. Conditions of synthesis of \((\text{Ag}_2\text{S})_x(\text{ZnS})\) heteronanostructures are described in detail in study [9].

The synthesized powders were washed and decanted. The synthesized samples were dried by sublimation methods in an Alpha 1-2 LDplus freeze dryer (Martin Christ) at an ice condenser temperature of -55°C (218 K).

| Sample | Composition | Reagent concentration in the reaction mixtures (mmol\(\cdot\)L\(^{-1}\)) | \(a_{\text{ZnS}}\) (nm) | \(D\pm0.5\) (nm) | \(h\pm1\) (nm) |
|--------|-------------|-------------------------------------------------|-----------------|-----------------|-----------------|
| 1      | \((\text{Ag}_2\text{S})_0.025(\text{ZnS})\) | \(\text{Zn(NO}_3\) | \(\text{Na}_2\text{S}\) | Trilon B | \(\text{Ag(NO}_3\) | \(\text{Na}_2\text{S}\) | \(\text{Na}_3\text{Cit}\) | | |
| 2      | \((\text{Ag}_2\text{S})_0.10(\text{ZnS})\) | 50 | 50 | 3.125 | 2.5 | 1.25 | 1 | 0.5375 | 10 | 4 |
| 3      | \((\text{Ag}_2\text{S})_0.25(\text{ZnS})\) | 50 | 50 | - | 25 | 12.5 | 5 | 0.5366 | 28 | 5 |
| 4      | \((\text{Ag}_2\text{S})_0.50(\text{ZnS})\) | 50 | 50 | - | 50 | 25 | 10 | 0.5363 | 30 | 5 |

Deposited dried sulfide nanopowders were examined by X-ray diffraction (XRD) method on a Shimadzu XRD-7000 diffractometer in \(\text{CuK}\alpha_{0.2}\) radiation. The determination of the crystal lattice
parameters and final refinement of the structure of the synthesized sulfide nanopowders were carried out with the use of the X’Pert Plus software suite [10].

The microstructure, particle size and element chemical composition of powders of (Ag$_2$S)$_x$(ZnS) heteronanostructures were studied by the scanning electron microscopy (SEM) method on a JEOL-JSM LA 6390 microscope coupled with a JED 2300 Energy Dispersive X-ray Analyzer and by the high-resolution transmission electron microscope (HRTEM) method on a JEOL JEM-2010 microscope.

In addition, the average particle size $D$ (more precisely, the average size of coherent scattering regions (CSR)) in synthesized nanopowders of (Ag$_2$S)$_x$(ZnS) heteronanostructures was estimated by XRD method from the diffraction reflection broadening using the dependence of reduced reflection broadening $\beta'(2\theta) = [\beta(2\theta)\cos\theta]/\lambda$ on the magnitude of scattering vector $s = (2\sin\theta)/\lambda$ [11, 12].

3. Results and Discussion

The XRD patterns of (Ag$_2$S)$_x$(ZnS) heteronanostructures are shown in Figure 1. For comparison, the XRD patterns of nanostructured Ag$_2$S with a particle size ~40 nm and nanostructured ZnS with a particle size ~4 nm are shown.

A quantitative analysis of XRD patterns of (Ag$_2$S)$_x$(ZnS) heteronanostructures and comparison with data [13, 14] has shown the presence of diffraction reflections of cubic ZnS and monoclinic Ag$_2$S. Diffraction reflections of Ag$_2$S and, especially, ZnS in XRD patterns of heteronanostructures are strongly broadened. It testifies to the small size of sulfide particles of which (Ag$_2$S)$_x$(ZnS) heteronanostructures consist.

![Figure 1. XRD patterns of (Ag$_2$S)$_x$(ZnS) heteronanostructures and nanostructured Ag$_2$S and ZnS.](image-url)
The observed set of diffraction reflections corresponds to cubic (space group $F\overline{4}3m$) zinc sulfide with structure of the sphalerite (zinc blende) type and to silver sulfide with monoclinic (space group $P2_1/c$) $\alpha$-Ag$_2$S acanthite structure. Crystal lattice constant $a_{ZnS}$ of ZnS is 0.5344-0.5398 nm.

According to the results of an energy-dispersive X-ray analysis, the contents of Zn, Ag and S in heteronanosstructure 1 are equal to $63.1\pm0.3$, $5.2\pm0.1$ and $31.7\pm0.2$ wt.%, and in heteronanostructure 2 to $53.4\pm0.3$, $17.6\pm0.2$ and $28.7\pm0.2$ wt.%, respectively. The contents of Zn, Ag and S in heteronanosstructure 3 are $40.9\pm0.3$, $33.9\pm0.2$ and $25.1\pm0.2$ wt.%, in heteronanostructure 4 are equal $29.6\pm0.2$, $48.6\pm0.3$ and $21.8\pm0.2$ wt.%, respectively. Considering the contents of elements determined and the ratios of reagent concentrations in reaction mixtures 1-4 (see Table 1), prepared heteronanostructures 1, 2, 3, and 4 have approximate compositions $(\text{Ag}_2\text{S})_{0.025}(\text{ZnS})$, $(\text{Ag}_2\text{S})_{0.10}(\text{ZnS})$, $(\text{Ag}_2\text{S})_{0.25}(\text{ZnS})$, and $(\text{Ag}_2\text{S})_{0.50}(\text{ZnS})$.

The formation of the heteronanostructure is confirmed by the HRTEM image of a nanoparticle (Fig. 2) obtained from the reaction mixture 2. It is observed that the central part of the nanoparticle is formed by silver sulfide, the interplanar distance of $\sim0.246$ nm coincides with the distance between the atomic planes (111) of silver sulfide with a monoclinic (space group $P2_1/c$) $\alpha$-Ag$_2$S acanthite structure. The surface of the nanoparticle is partially covered with a layer of cubic zinc sulfide: the observed interplanar distance of $\sim0.311-0.312$ nm corresponds to the distance between the atomic planes (111) of cubic (space group $F\overline{4}3m$) ZnS (Fig. 2). The size of Ag$_2$S particle is 15 nm, the size of ZnS particles is about 4 nm and consistent with the size estimated from XRD data (see Table 1).

![HRTEM image of a heteronanoparticle](image)

**Figure 2.** HRTEM image of a heteronanoparticle obtained from the reaction mixture 2. The central part of the nanoparticle is formed by Ag$_2$S, and the surface of the nanoparticle is partially covered with a layer of cubic ZnS. The inset presents the EDX spectrum of $(\text{Ag}_2\text{S})_{0.10}(\text{ZnS})$ heteronanostructure.

Some particles of the heteronanostructures synthesized represent plate-like nanoparticles of silver sulfide with the sizes up to 10 nm and more, which consist from disoriented crystal blocks with the sizes from 2 to 5 nm. Particles of silver sulfide are covered partially by more thin lamellar nanoparticles of cubic zinc sulfide.

Thus, the proposed two-stage chemical co-deposition of Ag$_2$S and ZnS sulfides allows synthesizing $(\text{Ag}_2\text{S})_x(\text{ZnS})$ heteronanostructures. Apparently, such synthesis procedure is also applicable to the preparation of heteronanostructures of other metal sulfides having different solubility.
4. Conclusions
A comparative study of chemical deposition of \((\text{Ag}_2\text{S})_x(\text{ZnS})\) heteronanostructures is carried out for the first time. The heteronanostructures were synthesized by chemical co-deposition of silver and zinc sulfides from aqueous solutions. Nanopowders of \((\text{Ag}_2\text{S})_x(\text{ZnS})\) sulfide heteronanostructures with different nanoparticle sizes and different phase compositions were obtained.

A change in the ratios of reagent concentrations allows one to control the size of \(\text{Ag}_2\text{S}\) nanoparticles in the prepared heteronanostructures in the range from 9 to 30 nm, and the size of the ZnS nanoparticles from 4 to 5 nm.

Acknowledgement
This study was supported by the Russian Science Foundation (grant no. 19-79-10101) through the Institute of Solid State Chemistry of the Ural Branch of the RAS.

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