Preparation and Properties of Nanocomposites in the Systems S–AgI and S–Ag2S–AgI in Dimethyl Sulfoxide

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Abstract. In this research work described synthesis of nanocomposites in the systems S–AgI and S–Ag2S–AgI in dimethyl sulfoxide (DMSO, (CH₃)₂SO) medium, and its some properties. Nanocomposites were obtained through the solvothermal synthesis at temperature range (T) 25–160°C. The initial solutions were prepared by dissolution of sulfur (S), silver nitrate (AgNO₃) and ammonium iodine (NH₄I) in DMSO. The final products were obtained through the simple exchange reactions between initial solutions. Using the X-ray phase analysis (XRD), energy dispersive X-ray analysis (EDAX) and scanning electron microscopy (SEM) the samples were tested on phase and elemental composition, particle size and morphology, respectively. The results of XRD revealed that nanocomposites represented by S and AgI for system S–AgI, and by S, AgI and Ag₂S for S–Ag₂S–AgI system. The EDAX analysis showed the presence in composition of the investigated samples such elements like S, Ag and I for both systems. The SEM images demonstrated that both systems have a heterogeneous structure, the particles represented by flat and irregular shape. The size of the particles for S–AgI is fluctuated from 100 to 50000 nm and for S–Ag₂S–AgI – from 90 to 4000 nm.

1. Introduction

Nanotechnology is an integral part of modern science. Production and implementation of nanoparticles (NPs) and nanocomposites (NCs) in different branches of science and technology is commonplace. Such a great interest in NPs is due to the fact that particles in the state of nanoscale acquire properties that cannot be manifested in their usual state (routine size). Being in the state of nanosize, particles show antimicrobial, electronic, magnetic and strength characteristics [1]. With regard to the use of inorganic nanoparticles, the range of applications varies from biomedicine to electronics [1, 2]. The choice of the S–AgI and S–Ag₂S–AgI inorganic system is explained by the fact that each of its components has a set of specific properties. This in turn can lead to the production of NCs with enhanced multifunctional characteristics.

Application of each component of our system has a wide range. S is one of the most abundant elements in nature with semiconductor properties and high biological activity. Thanks to this features S, it allotropic and nano state, widely applied in agriculture, electronics, biochemistry, medicine [3–5]. Ag–NPs are attractive for various fields of science and technique, due to getting of novel and improved properties in comparison with bulk Ag [6]. For example, Ag–NPs has such features, like electrical conductivity, chemical stability, catalytic activity, photocatalytic activity and antimicrobial properties [6, 7]. Nanocrystalline silver halides (AgX; X = Cl, Br, I) are semiconductors with indirect and direct band gap [8] and photosensitivity. Such properties give possibility to use AgX in photographic films and as photocatalysts [8–12]. However, as was mentioned at [12] the pure AgI nanostructures inclined to photo-reduction under visible light irradiation if no sacrificial reagent is supplied. The resolution of this problem is obtaining of composites with AgI or modification of surface of bulk material, which lead to the increasing of stability of the substance [12]. Ag₂S bulk material and Ag₂S–NPs also attractive for different fields, due to its antimicrobial, semiconductor, fluorescent, photocatalytic and other properties [13–16].
As for the methods for obtaining NCs, today there are no literature sources for obtaining the systems $S^{-}AgI$ and $S^{-}Ag_{2}S^{-}AgI$. However, there are many methods of production of the individual materials, $NPs$ or quantum dots of each component of our system or in combination with other precursors. In [17] was used 3D TiO$_2$ as suitable bases for fabrication a visible-light-induced 3D AgI@TiO$_2$ nanophotocatalyst. This composition revealed good photocatalytic properties and stability. Another compound with the Ag$^{-}$AgI/Al$_2$O$_3$ system was prepared by deposition-precipitation and photoreduction methods. The system exhibited ability to the degradation and mineralization of toxic persistent organic pollutants [18]. In research [19] was obtained AgI–Ag$_2$S heterostructure with enhanced photothermal and optical absorption properties; this heterostructure was more efficient than AgI and Ag$_2$S separate $NPs$. In [20] was developed AgCl–Ag$_2$S–NCs via a simple one pot hydrothermal route, with enhanced photocatalytic properties. The study [11] was devoted to the obtaining of the AgI–Ag$_2$S@C$_3$N$_4$–NCs with ability to degradation of aqueous pollutants. Also Ag$^{-}$ and Ag$_2$S–$NPs$ were studied on denitrification in sediments [15]. In study [21] was synthesized Ag$^{-}NPs$ in solutions of native and soluble starches in DMSO medium. As the result, Ag$^{-}NPs$ showed good stability and DMSO solution of soluble starch was characterized by better reductive activity than the native starch solution.

As can be seen, the development of the synthesis technology of NCs based on AgI and Ag$_2$S has a considerable interest. Moreover, the composites of the composition $S^{-}AgI$ and $S^{-}Ag_{2}S^{-}AgI$ have not yet been obtained. Therefore the aim of this study was preparation of the $S^{-}AgI$ and $S^{-}Ag_{2}S^{-}AgI$–NCs in DMSO medium. Based on this aim the following tasks were set: development of the modes of the synthesis and study of the possibility of obtaining of NCs in DMSO. The synthesized NCs were studied by means of XRD, SEM and EDAX.

2. Materials and methods

2.1 Materials

AgNO$_3$ (>99.8%, Sigma Aldrich), and chemically pure (LaborPharma) NH$_4$I, S and DMSO were used. For the preparation of water solutions and washing of the samples we used water purified by purification system Smart2Pure (Thermo scientific).

2.2 Synthesis of $S^{-}AgI$

At the first stage of the synthesis there was preparing of the initial solutions at room temperature. According to the calculations for obtaining of the AgI 1.4468 g of AgNO$_3$ was dispersed into 50 mL of DMSO and stirred until full dissolution. The same operations were made with the 2.4680 g of NH$_4$I. The amount of NH$_4$I was doubled to avoid the formation of Ag$_2$S. When the initial solutions are ready, there are goes the obtaining of S solution in DMSO. The process occurs with help of installation which consist of three-neck-flask, backflow condenser, thermometer, silicone oil bath and magnetic stirrer. 100 mL of DMSO surged into the three-neck-flask and then 1 g of S is added. When all components were added, the system was exposed to the constant stirring (400 rpm) and gradual heating. S started dissolve at 110°C and at 120°C totally goes into the DMSO solution. When the mark T reached 120°C the heating is stopped. When the T of the reactional mixture reached ~50°C there are goes alternately adding of initial solutions of AgNO$_3$ and NH$_4$I. As soon as all the solutions were added, 150 mL of ultrapure water was added to the mixture in order to extract the S. Then the product of the synthesis was precipitate on centrifuge ROTINA380R for 15 minutes and at a speed 4000 rpm and washed by ultrapure water 2 times. Eventually the samples had been dried at 50°C, for 15-20 hours.

2.3 Synthesis of $S^{-}Ag_{2}S^{-}AgI$

As at the first method, which was described at previous paragraph, solutions of AgNO$_3$ and NH$_4$I were prepared in DMSO at room temperature. According to the stoichiometric calculations 1.0282 g of AgNO$_3$ was dissolved in 50 mL of DMSO and 0.3532 g of NH$_4$I in 50 mL of DMSO. When the initial solutions are ready, there are goes the obtaining of S solution in DMSO. In this method there was used the same installation which was mentioned above. All operations repeated like at first method, but the reactional system heated gradually to 160°C. When T reached 160°C there are goes alternately adding of initial solutions AgNO$_3$ and NH$_4$I. When initial solutions were added, the
reactional system was cooled at room T during 12 hours. The finishing stage involved the precipitation of sediment and drying at previous paragraph.

2.4. Instruments

For the structural characterization of the investigated samples was a conducted XRD. The XRD of the samples was carried out using X-ray diffractometer Rigaku MiniFlex 600 (CuKα radiation, \( \lambda = 1.54056 \) nm). Identification of the sample was made using the JCPDS−PDF2 database. For determination of the S was used literature source [22]. The SEM-analysis was conducted with help of scanning electron microscope Quanta 200i 3D, equipped by EDAX for investigation of the particle size and its morphology and elemental composition. The microscope was operated at an accelerating voltage 15 kV, a conductive carbon adhesive tape served as substrate for the samples.

3. Results and discussions

According to the XRD analysis the S−AgI nanocomposite is consist of S (S₈ form) and hexagonal β−AgI (figure 1). The black line is the experimental sample of the S−AgI−NCs. The red columns is S and green columns is AgI. As can be seen from the XRD patterns the intensive peaks values at 2 theta (2θ) = 22.30, 23.70, 25.35, 32.75, 39.20, 42.65 and 46.35° correspond to the reflections (100), (002), (101), (102), (110), (103) and (112) of β−AgI (JCPDS file no. 09-0374), respectively. Weak peaks 52.00, 59.30, 71.05 and 73.40° also correspond to the reflections (202), (203), (210), (300), (213) and (302) of β−AgI (JCPDS file no. 09-0374), respectively. More noticeable high peak for S₈ [22] is 23.10° and low peaks are 11.45, 15.40, 26.70, 27.75, 28.65, 31.40, 34.25, 34.90, 35.90, 37.05, 37.80 and 56.70°. Those peaks can be indexed to the reflections (222) and (111), (113), (311), (313), (044), (400), (333), (244), (317), (422) and (624), accordingly.

The crystalline size was calculated using Debye-Scherrer equation [23]. According to the calculations the average crystalite size of S−AgI−NCs sample is about 140 nm.

Figure 2 shows the XRD patterns for S−Ag₂S−AgI. According to the results of analysis it can be seen that the sample has a characteristic peaks of S₈, mainly monoclinic α−Ag₂S (acanthite) and β−AgI. The black line corresponds to the experimental results, the red columns is S, the blue is Ag₂S and the green is AgI. The most distinct peaks for AgI are 22.40, 23.70, 32.65, 39.25, 42.75, 46.35, 71.15 and 76.05° correspond to the reflections (100), (002), (102), (110), (112), (300) and (302) of the β−phase, respectively. The Ag₂S (JCPDS file no. 14-0072) exhibit the weak diffraction peaks nearly 29.00, 31.50, 34.50, 36.81, 37.70 and 43.45°, which were indexed as (111), (−112), (−121), (121), (−103) and (200) diffraction plane, respectively. The appearance of such peaks like 23.10 and 27.75° is attributed by (222) and (206) reflections of the S₈ [22]. The crystalline size of the S−Ag₂S−AgI−NCs was calculated and the average size was nearly 80 nm.
EDAX analysis confirmed the presence of elements, which were founded by XRD for both systems. According to EDAX the S–AgI sample consists of S, Ag and I (figure 3ab and table 1).

Pointed investigation shows that sample represented by light particles (in basis) and also there can be seen the dark flat particles of big sizes (figure 4ab). Elemental composition of that area (figure 4a and table 2) revealed that the dark particle is consist of S on 87.42 At%, remaining 6.44 and 6.15 At% are Ag and I (the light small particles, which settled on the surface of the S (figure 4b), respectively.

### Table 1. The percentage data of the EDAX analysis of the S–AgI

| Element | Wt% | At% |
|---------|-----|-----|
| S       | 4.08| 13.43|
| Ag      | 45.81| 44.86|
| I       | 50.11| 41.71|

### Table 2. The percentage data of the EDAX analysis of the dark area of the S–AgI

| Element | Wt% | At% |
|---------|-----|-----|
| S       | 65.54| 87.42|
| Ag      | 16.23| 6.44|
| I       | 18.23| 6.15|
Elemental composition of the S–Ag₂S–AgI in general represented by S (13.31 At%), Ag (45.38 At%) and I (22.35 At%), see figure 5 and table 4.

Figure 5. EDAX of the S–Ag₂S–AgI: a) the spectra; b) the area from which the data was obtained

Table 3. The percentage data of the EDAX analysis of the S-Ag₂S-AgI

| Element | Wt% | At%  |
|---------|-----|------|
| O       | 3.59| 18.97|
| S       | 5.04| 13.31|
| Ag      | 57.85| 45.38|
| I       | 33.52| 22.35|

As can be seen on the figure 6b the S–Ag₂S–AgI sample also presented in some areas by dark and flat particles. The analysis of that zone proved that the particle consists of 91.90 At% of S (table 5).

Figure 6. EDAX of the S–Ag₂S–AgI (black area): a) the spectra; b) the area from which the data was obtained

Table 4. The percentage data of the EDAX analysis of the S-Ag₂S-AgI (black area)

| Element | Wt% | At%  |
|---------|-----|------|
| O       | 4.21| 8.10 |
| S       | 95.79| 91.90|

After phase investigation there was made characterization of morphology of the samples and study of its particle size. The images of the S−AgI sample are shown on the figure 7.

![Figure 7. SEM-analysis of the S−AgI (a, b, c)](image)

According to the SEM the sample is heterogeneous; the particles are represented by both large and small sizes (figure 7a). The large particles of dark colour has the size about 2-5 µm. More detail study of the dark particles (figure 7b) revealed that on its surface settled the light particles of AgI (100-1000 nm) according to EDAX. The size of the S−AgI particles fluctuated from ~100 nm to 5 µm (figure 7abc). As for the morphology of the sample, it is obvious that the dark particles of S (figure 4b) are flat and light particles are mainly oval or sphere shape with a smooth surface.

The images of the S−Ag2S−AgI sample are shown on the figure 8.

![Figure 8. SEM-analysis of the S−Ag2S−AgI obtained in DMSO medium (a, b, c)](image)

The S−Ag2S−AgI also has non-uniform mass (figure 8ab). There are also present light (figure 8a) and dark (figure 8c) particles. The size of the particles varies from ~90 nm to 4 µm. In general particle has irregular shape.

In both cases there is a strong defect of crystallites and coalesce of small crystallites, which complicates the determination of real sizes of particles. These syntheses were carried out at high temperatures, which make it hard to control the size of the resulting particles.

Also, the complex composition of the system leads to the difficulty of controlling the particle size, since each of the constituent components has own "behavioral" features. In other hand, according to the XRD and SEM analyses, both methods can give nanosized particles; the problem is that small crystallites coalesce with each other and form large agglomerates. Stabilization of the particles can serve as solution of the mentioned problem.

In addition, the use of DMSO as a solvent makes it possible to apply a wide temperature range for synthesis. Thus, it can allow not to be tied to one temperature regime. DMSO is an aprotic bipolar solvent. It is widely used in medicine, biology and pharmacy [24]. Therefore, there is no need to be afraid of using this solvent from an environmental point of view.
4. Conclusion

In this study, the synthesis of S−AgI and S−Ag₂S−AgI nanocomposites was carried out for the first time. The synthesis passed with using precursor solutions in dimethyl sulfoxide, at temperatures above 120°C. By XRD it was established that obtained nanocomposites have characteristic diffraction peaks of S in S₈ form and β−AgI for S−AgI, and S₈, α−Ag₂S and β−AgI for S−Ag₂S−AgI.

Owing to the EDAX analysis was confirmed the presence of S, Ag and I in both cases, and the pointed EDAX showed that dark flat particles represented by S. The EDAX spectra of S−Ag₂S−AgI nanocomposite revealed the presence of the O, this indicates impurity of obtained crystallites.

The XRD also showed that the S−AgI has an average size of the particles equal to 140 nm, meanwhile S−Ag₂S−AgI – 80 nm. However, SEM analysis did not confirm this data. According to the SEM the size of the S−AgI particles is about from 100 nm to 5 μm and S−Ag₂S−AgI particles is about from 90 nm to 4 μm. An attempt was made to explain the differences in the results of these methods.

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