Self-Assembly of Ag₂S Colloidal Nanoparticles Stabilized by MPS in Water Solution

Svetlana V. Rempel,* Yulia V. Kuznetsova, and Andrey A. Rempel

ABSTRACT: Self-assembly of colloidal Ag₂S nanoparticles (NPs) was studied in the presence of (3-mercaptopropyl)trimethoxysilane (MPS). Solutions with different molar ratios of Ag₂S/MPS were prepared. The appearance of nano- and microtubes was detected. Self-organized NPs were studied with optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and high-resolution transmission electron microscopy (HRTEM). Silicon nuclear magnetic resonance spectroscopy (²⁹Si NMR) was used to study polycondensation of MPS molecules. Geometrical parameters of the nano- and microtubes depended on the molar ratio of Ag₂S/MPS. The scheme and mechanism of self-assembly of Ag₂S NPs in nanotubes in the presence of MPS were proposed. The effect of MPS on the preservation of the initial stoichiometry of Ag₂S NPs was discussed.

INTRODUCTION

The ability of nanoparticles (NPs) to self-assemble into superstructures under certain conditions is promising to design novel optical, catalytic, and magnetic devices, as well as to be used in medicine, pharmaceutics, and industrial processes. A new concept in designing a wide range of materials has appeared recently, which is called nanoarchitectonics. Self-assembly processes play a crucial role in this concept. Numerous complex mechanisms and a comprehensive approach are necessary for target architectures. Thus, self-assembly is currently one of the key topics in physics, chemistry, and mathematics.¹⁻⁷

For NPs to be successfully used, they should be placed into a matrix or be stabilized with inorganic/organic materials. Organic ligands play an important role not only in the stabilization of inorganic NPs but also in the formation of two- and three-dimensional self-organized assemblies of NPs in ref 4. For medicine and biology, of interest are self-assembled structures based on inorganic NPs with biocompatible/bioactive organic molecules; for example, nanomaterials based on self-assembly of charged polysaccharides, namely, chitosan and alginate, onto inorganic NPs can be used for efficient disinfection and microbial control. A promising material that can be used to stabilize and form target architectures is (3-mercaptopropyl)trimethoxysilane (MPS). The studies in refs 13–15 report about the assembly of mono- and two-dimensional (2D) structures based on MPS onto which different agents are mobilized to create immunosensors.

Silver sulfide (Ag₂S) NPs have attracted much attention due to their potential applications in photoconductors, solar cells, near-infrared photodetectors, biology, medicine, etc.¹⁶⁻²⁸ Under certain conditions, Ag₂S NPs are also capable of self-assembly.²⁹⁻³¹ In ref 25, it was shown that Ag₂S nanowires can be utilized as a catalyst for the electrochemical CO₂ reduction reaction.

Thus, to develop nanoarchitectures of novel materials, it is interesting to consider self-assembly processes in the Ag₂S/MPS system. In ref 32, a simple one-step synthesis of Ag₂S NPs in water solution with MPS as capping molecules was reported. The aim of the present study was to investigate the effects of different concentrations of MPS on self-assembly of Ag₂S colloidal NPs.

RESULTS AND DISCUSSION

The hydrodynamic diameter of NPs in solution was studied right after synthesis, 1 day later, and then 14 days after the synthesis (Table 1).

Immediately after the synthesis, the hydrodynamic radius of NPs was about 60 nm for all concentrations. The average NP diameter in the solution with the least concentration changed insignificantly with time; as the MPS concentration increased, the NP diameter increased almost 2-fold, and an additional fraction of micrometer-sized agglomerates appeared.

Received: April 30, 2020
Accepted: June 18, 2020
Published: July 2, 2020
by increasing the MPS to Ag₂S ratio from 0.25 up to 1 results in a significant increase in absorption, which starts at about 400 nm, and curves monotonically rising toward the short-wave side. An increase in the optical absorption, which indicates the sedimentation of NPs due to agglomeration.

Table 1. Hydrodynamic Diameter of Ag₂S NPs versus Ag₂S/MPS Molar Ratio and Time

| sample       | Ag₂S/MPS molar ratio | 0 days  | 1 day  | 14 days |
|--------------|-----------------------|--------|--------|---------|
| Ag₂S–MPS 0.25| 1:0.25                | 67 ± 24| 81 ± 25| 83 ± 27 |
| Ag₂S–MPS 0.5 | 1:0.5                 | 66 ± 21| 68 ± 21| 104 ± 24 (96%) |
| Ag₂S–MPS 1   | 1:1                   | 58 ± 20| 80 ± 26| 137 ± 28 (90%) |

Figure 1. Number size distribution of Ag₂S NPs in water solution stabilized with different concentrations of MPS.

Figure 2. Optical absorption of aqueous solution that contains Ag₂S NPs covered by MPS.

Optical properties of colloidal solutions after synthesis have been studied. Figure 2 presents the UV–vis–NIR optical absorption spectrum of the colloidal solution after synthesis that contains Ag₂S NPs covered by MPS. The colloidal Ag₂S absorption spectra in the 230–1250 nm region are represented by curves monotonically rising toward the short-wave side. An intensive increase in absorption, which starts at about 400 nm, is detected for all samples. Increasing the MPS concentration by increasing the MPS to Ag₂S ratio from 0.25 up to 1 results in a significant increase in optical absorption, which indicates the sedimentation of NPs due to agglomeration.

Silicon nuclear magnetic resonance spectroscopy (²⁹Si NMR) was used to establish the state of stabilizer molecules (monomers, hydrolyzed monomers, dimers, and short or long polymers) and to clarify the formation of agglomerates of Ag₂S NPs stabilized by MPS. ²⁹Si NMR spectra were obtained on the following samples: MPS (initial chemical reagent), MPS in alcohol, MPS in aqueous alcoholic solution, and an aqueous solution of Ag₂S NP stabilized by MPS.

The MPS monomer has one line in the ²⁹Si NMR spectrum with a chemical shift of about −42.56 ppm. After addition of alcohol, hydrolysis of MPS molecules begins, which leads to a change in the chemical shift to −40.07...39.95 ppm. At the same time, there is a signal from the nonhydrolyzed monomer MPS, however, with a shift of −41.7 ppm, which indicates incomplete hydrolysis during the measurement (Figure 3).

The difference from the value of the initial MPS (which coincides with that in the published data) can be caused by the solvent used (chloroform-d). The appearance of a line in the region of −48.5...−49.5 ppm indicates the formation of dimers. A weak signal in the region of −55...−80 ppm indicates the beginning of the process of polycondensation and the formation of polymer chains. At the same time, even after 14 h after the addition of water, a signal of −39.95 ppm is present, which may be associated with a small amount of water, which is sufficient for the hydrolysis of MPS but not enough for complete condensation and polycondensation of molecules. The signal at −50.84 ppm after the addition of water requires further analysis.

No signal was detected on the sample with Ag₂S NPs even after 30 h of collecting the statistics. This is due to a low concentration of MPS used for stabilization. The work on the synthesis of a stable sample with a higher concentration of MPS is underway.

After the obtained solutions were kept under normal conditions for one month, all of the samples exhibited changes in the form of precipitates or bulk suspension. The precipitate and the solution were examined using optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and HRTEM methods.

In the sample with the initial Ag₂S/MPS ratio equal to 1:0.25, a dark precipitate was found at the bottom of the vessel. When agitated, the particles were distributed in the solution, but, at the same time, they seemed partly bound to each other. While investigating the precipitate by the HRTEM method, agglomerates were observed. The agglomerates aggregate into a cluster of such chains.
At the Ag$_2$S/MPS ratio of 1:0.5, we also observed a precipitate at the bottom of the vessel, and transparent light brown conical formations were attached to the surface of the vessel (Figure 5a). Analysis of the precipitate using optical microscopy and SEM methods revealed hollow tubes with a diameter of about 1.5 μm. It is not possible to find the length of the tubes because they are interlaced into a loose ball. From the results of the analysis using the EDX method, it can be concluded that the tubes consist of Ag$_2$S and MPS (Figure 5).

Analysis of the precipitate with the HRTEM method revealed that the phase composition is analogous to that in the previous case. The agglomerates represent a cellular structure consisting of large chains; some chains, preserving a curved form, become thicker and contain more NPs than in the sample with the 1:0.25 ratio (Figure 6). In addition, fragments of tubes were observed at whose boundaries Ag$_2$S NPs were accumulated. The tubes were about 20 nm thick.

When the ratio of the initial Ag$_2$S/MPS components was 1:1, a suspended porous formation of interlaced light brown tubes was observed after a month. When a large amount of solution was synthesized at the same ratios of components, a suspended cloud of greater size was formed (Figure 7).

The results of the analysis of the samples with the HRTEM method demonstrated a developed matrix. Tubes with a diameter of 200–250 nm and a wall thickness of ~20 nm were clearly observed. A matrix with individual NPs was located between the tubes. As in the previous cases, NPs of metallic Ag can be observed along with Ag$_2$S NPs. Large (to 50 nm)
Figure 5. Optical images (a, b) and SEM images (c, d) of microtubes from the precipitate (Ag₂S/MPS molar ratio 1:0.5). The inset of (c) is EDX of the microtubes.

Figure 6. HRTEM images of the Ag₂S/MPS precipitate (Ag₂S/MPS molar ratio 1:0.5).

Figure 7. Optical image of the Ag₂S/MPS precipitate (Ag₂S/MPS molar ratio 1:1).

Figure 8. HRTEM images of the nanocores (Ag₂S/MPS molar ratio 1:1).
smaller (3−20 nm) NPs of both fractions may consist of smaller crystallites. The content of metallic silver was insignificant, since it was not detected by X-ray photoelectron diffraction (XPD) analysis of the precipitates. Along with small chains, the solution contained nanorods of AgS (10 nm thick and up to 300 nm long), which were modified under the action of an electron beam (Figure 8).

Thus, self-assembly of NPs into tubes was found in the presence of MPS. The thickness of the tube walls is about 20 nm, and the diameter depends on the initial content of MPS and is 200−300 nm; however, it can reach as much as 1.5 μm. The NPs of the dispersed phase are incorporated into the matrix. An increase in the MPS content leads to the formation of loose balls consisting of tubes of indefinite length. At the maximal concentration of MPS, AgS nanorods are also detected in the solution. The modeling performed in ref33 on the basis of the concepts of the DLVO (Derjaguin−Landau−Verwey−Overbeek) theory of aggregate stability of lyophobic disperse systems shows that individual NPs are united into chains due to the synchronous action of van der Waals and electrostatic forces. The chains are capable of uniting into tubular structures with time.

Thus, the chain structures consisting of MPS and NPs play a key role in the subsequent formation of microtubes. Increasing the relative content of MPS promotes the growth of such chains in length and width.

Based on the studies performed, it is possible to represent a scheme of the process of self-assembly of AgS NPs in the presence of MPS (Figure 9).

At the moment right after synthesis, AgS NPs stabilized by MPS are formed, and these NPs are about 60 nm in hydrodynamic diameter. Then, in the course of time, the particles grow due to their incorporation into chains and increase in their lateral dimensions as a result of polycondensation of MPS. In 14 days, the size of the main fraction becomes as much as 83, 104, and 137 nm for the ratios 1:0.25, 1:0.5, and 1:1, respectively. The size of the main fraction grows with increasing initial content of MPS. The process of polycondensation of MPS continues in the subsequent periods and leads to the formation of self-assembled structures in the form of hollow tubes AgS/MPS and Ag nanorods. At the AgS/MPS ratio of 1:1, the nanotubes become 1.5 μm in diameter, and clusters of nanotubes continue to exist for a long time in the solution in the form of a loose suspension until complete evaporation of the solvent. The mechanism of formation of nanorods in the presence of MPS requires further research on AgS.

One more feature connected with the presence of MPS is noteworthy. Silver sulfide is prone to nonstoichiometry even in the low-temperature α-Ag2S monoclinic phase,34 which results in the AgS−xS compound and the appearance of defects. The main defects are interstitial silver ions (IAg), sulfur vacancies (VS), and substitutional defects (SAg). Owing to such a structure, AgS NPs are easily reduced to Ag under different external actions. The presence of Ag NPs in colloidal solutions of AgS with different stabilizers is a problem if it is necessary to produce a monophase material. Organic stabilizers, for example, sodium citrate Na3C6H5O7, lead to a considerable reduction of silver sulfide to pure silver.28,35 Ag NPs were found in the examined samples with the use of the HRTEM method, while metallic Ag was not detected using the XPD method. The content of Ag may be below the sensitivity of this method. On the whole, the presence of metallic Ag was insignificant. Under the action of an electron beam, AgS nanorods were modified as described in an earlier work.27 The rounded NPs enclosed into the MPS matrix remained stable. Thus, the MPS shell protects the AgS NPs from reduction to metallic Ag much better under the action of external factors, that is, it contributes to the preservation of initial stoichiometry.

**CONCLUSIONS**

The effect of MPS on the processes of stabilization and self-assembly of AgS NPs in aqueous colloidal solutions at the initial point of time and in long-term investigations was considered in this work. A scheme of nanotube formation was proposed. At the first stage after synthesis, AgS NPs covered with an MPS shell are formed. When the relative content of...
MPs and the concentration of Ag₅S/MPS increase due to polycondensation of MPS molecules, the process of self-assembly leads to the formation of microtubes from 200 nm to 1.5 μm in size, with a wall thickness of about 20 nm and indefinite length. These microtubes are interlaced into a ball. MPS plays a key role in the self-assembly. By varying the relative concentration of MPS it is possible to control the tube size. At the maximal concentration of MPS, Ag₅S nanorods are also observed in the solution. The MPS matrix protects Ag₅S NPs from the action of radiation, electron beam, and time factor. The results of the study of the self-assembly in the Ag₅S/MPS system can be useful for the development of nanoarchitectonics of novel functional materials.

**MATERIALS AND METHODS**

3-Mercaptopropyl-trimethoxysilane (HSC₃H₂Si(OCH₃)₃, >95%), sodium sulfide (Na₂S) from Sigma Aldrich, ethanol (EtOH), and silver nitrate (AgNO₃) from the domestic market were used. All of the chemicals were of analytical grade (ACS) and were used without further purification. Distilled water was used to prepare the sample. Ag₅S NPs were synthesized in a water solution by using the chemical condensation technique following the stoichiometric Ag-to-S content in the Ag₅S/MPS ratio to more than 1:1 results in agglomeration and precipitation. In contrast to ref29, the MPS content in the Ag₅S/MPS ratio to more than 1:1 results in agglomeration and precipitation. In contrast to ref29, the MPS to Ag₅S NP molar ratios of 0.25, 0.5, and 1 were used in the experiments to study the effect of the stabilizing agent in the present work.

The hydrodynamic diameter, Dᵥ, and number size distribution of Ag₅S NPs in the solution were measured using dynamic light scattering on a Zetasizer Nano ZS facility (Malvern Panalytical Ltd.) at 25 °C and a wavelength of 633 nm. All of the measurements were repeated three times for good statistics of the results. UV–vis–NIR optical characterization of the synthesized Ag₅S–MPS solutions was carried out using a FSS spectrophotometer (Edinburgh Instruments) at ambient temperature in the wavelength range from 230 to 1250 nm. Optical images were obtained by using a Leica 2500M DM microscope (Carl Zeiss). The images and EDX of the synthesized samples were obtained on a SIGMA VP (Carl Zeiss) scanning electron microscope (SEM) under high vacuum using an InLens detector.

HRTEM images of the synthesized Ag₅S–MPS solutions were recorded on a JEOL JEM-2010. The colloidal solutions of Ag₅S NPs were dropped on a copper grid and dried in air at room temperature for examination. The phase components were identified with fast Fourier transformation (FFT) of the HRTEM images. An X-ray diffraction analysis (XRD) study of the precipitate was performed on a STADI-P diffractometer (STOE, Germany). A silicon nuclear magnetic resonance (²⁹Si NMR) study of the MPS behavior in solution was performed on a Bruker Advance Neo 600 Spectrometer at 119 MHz at 298 K. Tetramethylsilane Si(CH₃)₄ (tetramethylsilane (TMS), 0 ppm) as the reference and chloroform-d (CDCl₃) as the solvent were used. For ²⁹Si NMR experiments, MPS concentrations of 3.15 g/L in a solution without NPs and 0.016 mg/L in a solution with NPs were used.

**AUTHOR INFORMATION**

**Corresponding Author**

Svetlana V. Rempel — Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russia; Ural Federal University, 620002 Ekaterinburg, Russia; orcid.org/0000-0002-8747-6719; Email: svetlana_rempel@phim.uran.ru; Fax: +7 343 374 4495

**Authors**

Yulia V. Kuznetsova — Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russia

Andrey A. Rempel — Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russia; Ural Federal University, 620002 Ekaterinburg, Russia; Institute of Metallurgy, Ural Branch of the Russian Academy of Sciences, 620016 Ekaterinburg, Russia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01994

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors are grateful to E. Y. Gerasimov, O. S. Eltsov, and I. D. Popov for their assistance. This work was supported by the RSF [project no. 19-73-20012].
assembled nanocapsules as antibacterial agent. Colloids Surf., B 2019, 181, 158–165.
(9) Meng, L.; Chen, W.; Tan, Y.; Zou, L.; Chen, C. P.; Zhou, H. P.; Peng, Q.; Li, Y. D. FeO₄ octahedral colloidal crystals. Nano Res. 2011, 4, 370.
(10) Zhu, L.; Shan, S.; Petkov, V.; Hu, W.; Kroner, A.; Zheng, J.; Yu, C.; Zhang, N.; Li, Y.; Luque, R.; et al. Ruthenium–nickel–nickel hydroxide nanoparticles for room temperature catalytic hydrogenation. J. Mater. Chem. A 2017, 5, 7869–7875.
(11) Zhu, L.; Jiang, Y.; Zheng, J.; Zhang, N.; Yu, C.; Li, Y.; Pao, C. W.; Chen, J. L.; Jin, C.; Lee, J. F.; et al. Ultrathin Nanoparticle-Supported Ru Nanoclusters with Ultrahigh Catalytic Activity. Small 2015, 11, 4385–4393.
(12) Zhu, L.; Yang, Z.; Zheng, J.; Hu, W.; Zhang, N.; Li, Y.; Zhong, C.-J.; Ye, H.; Chen, B. H. Decoration of Co/Co₃O₄ nanoparticles with Ru nanoclusters: a new strategy for design of highly active hydrogenation. J. Mater. Chem. A 2015, 3, 11716–11719.
(13) Zhang, Y.; Luo, H. Q.; Li, N. B. Hydrogen peroxide sensor based on Prussian blue electrodeposited on (3-mercaptopropyl)trimethoxysilane polymer-modified gold electrode. Bioprocess Biosyst. Eng. 2011, 34, 215–221.
(14) Cai, M.; Ho, M.; Pemberton, J. E. Surface Vibrational Spectroscopy of Alkylsilane Layers Covalently Bonded to Monolayers of (3-Mercaptopropyl)trimethoxysilane on Ag Substrates. Langmuir 2000, 16, 3446–3453.
(15) Zhang, L.; Qi, K. The Fabrication of an Amperometric Immunosensor Based on Double-Layer 2D-Network (3-Mercaptopropyl)trimethoxysilane Polymer and Platinum-Prussian Blue Hybrid Film. Bull. Chem. Soc. Jpn. 2018, 91, 368–374.
(16) Cui, C.; Li, X.; Liu, J.; Hou, Y.; Zhao, Y.; Zhong, G. Synthesis and functions of Ag₃S nanostructures. Nanoscale Res. Lett. 2015, 10, No. 431.
(17) Perpepita, A. S.; Smirnov, M. S.; Ovchinnikov, O. V.; Latsyhev, A. N.; Kotko, A. S. Thermostimulated luminescence of colloidal Ag₃S quantum dots. J. Lumin. 2018, 198, 357–363.
(18) Robinson, D. A.; White, H. S. Electrochemical Synthesis of Individual Core@Shell and Hollow Ag/Ag₃S NP. Nano Lett. 2019, 19, 5612–5619.
(19) Cai, M.; Ding, C.; Cao, X.; Wang, F.; Zhang, C.; Xian, Y. Label-free fluorometric assay for cytochrome c in apoptotic cells based on near infrared Ag₃S quantum dots. Anal. Chim. Acta 2019, 1056, 153–160.
(20) Chen, G.; Tian, F.; Zhang, Y.; Zhang, Y.; Li, C.; Wang, Q. Tracking of Transplanted Human Mesenchymal Stem Cells in Living Mice using Near-Infrared Ag₃S Quantum Dots. Adv. Funct. Mater. 2014, 24, 2481–2488.
(21) Shen, Y.; Lifante, J.; Ximendes, E.; Santos, H.; Ruiz, D.; Juárez, B. H.; Gutiérrez, I. Z.; Vera, V. T.; Retama, J. R.; Rosal, E. M.; et al. Perspectives for Ag₃S NIR-II NP in biomedicine: from imaging to multifunctionality. Nanoscale 2019, 11, 19251–19264.
(22) Jang, J.; Cho, K.; Lee, S. H.; Kim, S. Synthesis and electrical characteristics of Ag₃S nanocrystals. Mater. Lett. 2008, 62, 1438–1440.
(23) Kumari, P.; Chandran, P.; Khan, S. S. Synthesis and characterization of silver sulfide NP for photocatalytic and antimicrobial applications. J. Photochem. Photobiol., B 2014, 141, 235–240.
(24) Wang, M.; Wang, Y.; Tang, A.; Li, X.; Hou, Y.; Teng, F. Optical properties and self-assembly of Ag₃S NP synthesized by a one-pot method. Mater. Lett. 2012, 88, 108–111.
(25) Zheng, C.; Qi, Z.; Chen, G. Silver sulfide quantum dots as sensitizer in self-cleaning of Bombyx mori silk fabrics with nano-titania. J. Text. Inst. 2016, 107, 1501–1510.
(26) Rempel, S. V.; Aleksandrova, N. N.; Kuznetsova, Yu. V.; Gerasimov, E. Yu. Influence of the size and charge of non-stoichiometric silver sulfide NP on their interaction with blood cells. Inorg. Mater. 2016, 52, 101–105.