Synthesis of Ag$_2$S colloidal solutions in D$_2$O heavy water

Stanislav I. Sadovnikov and Aleksandr I. Gusev

For the first time, colloidal solutions of silver sulfide are synthesized by chemical deposition from solutions of silver nitrate and sodium sulfide in heavy water D$_2$O. In the synthesis, sodium citrate was used as a stabilizer. The sizes of Ag$_2$S quantum dots in colloidal solutions were estimated by dynamic light scattering and transmission electron microscopy. The size of silver sulfide quantum dots in colloidal solutions in heavy water that were prepared from reaction mixtures with different concentrations of reagents is from 3 to 19–20 nm. An increase in the concentration of silver nitrate and a decrease in the concentration of sodium citrate in the initial reaction mixtures lead to a small increase in the size of Ag$_2$S quantum dots in the synthesized colloidal solutions. Colloidal silver sulfide solutions synthesized using D$_2$O heavy water retain the stability and constant size of the nanoparticles after storage for more than 100 days. The calculated exciton diameter for Ag$_2$S is about 3 nm, and is consistent with experimental observations.

1. Introduction

Ag$_2$S QDs can be used in infrared detectors, in resistance-switches and nonvolatile memory devices. Ag$_2$S QDs can be used in the manufacture of nanocomposite photocatalysts and materials for conversion of solar energy into electrical energy. Stable Ag$_2$S QDs possess high fluorescence emission from the UV to NIR region.

Nanostructured silver sulfide including quantum dots has been produced by different methods such as hydrochemical deposition, template method, sol–gel method, synthesis in microemulsions, as well as by sonochemical, hydrothermal, solvothermal, electrochemical, microwave and other techniques. Detailed description of various methods for the synthesis of nanostructured silver sulfide is given in review. However, many of these methods are not universal and allow synthesis of nanostructured silver sulfide only in one form: either nanopowders, or films, or heteronanostructures. Bad control of the size and non-uniform broad size distribution of nanoparticles, use of multistage (3–4 stages) sequential processes, complicated technique and special defenders, the raised temperatures, rare and expensive reagents are the main disadvantages of many preparation methods of nanostructured Ag$_2$S.

Different synthetic methods of Ag$_2$S QDs have been summarized in review. Recently a group of Prof. J. G. Tang, using a reverse microemulsion approach, synthesized uniform 3–8 nm Ag$_2$S nanoparticles.

The chemical deposition from aqueous solutions is the most simple and widespread method used for the synthesis of nanocrystalline sulfide powders and colloidal solutions of sulfide quantum dots including Ag$_2$S QDs.

Usually colloidal solutions of silver sulfide synthesize by hydrochemical deposition from aqueous solutions of silver nitrate AgNO$_3$ and sodium sulfide Na$_2$S. Solution of trisodium citrate dihydrate (sodium citrate) Na$_3$C$_6$H$_5$O$_7$·2H$_2$O = Na$_3$Cit uses as an electrostatic stabilizer, disodium salt of ethylenediaminetetraacetic acid (Trilon B) is used as the complexing agent. Chemical deposition with using sodium citrate Na$_3$Cit is a well-known, simple and reliable universal green method which allows preparing colloidal solutions of Ag$_2$S QDs.

Not only homogeneous size distribution, but also the exact control of the real form (sphere, ellipsoid etc.) of Ag$_2$S QDs is required for their application in electronic and optoelectronic devices.

Modern diagnostics of nanosystems uses various types of radiation to obtain information about the structure of nano-objects in volume and on surfaces. The special properties of low-energy neutrons with a wavelength of about 0.15 nm (1.5 Å), which include thermal and cold neutrons, make it possible to effectively use their scattering in studies of solids, liquids, and colloidal systems. Neutron diffraction methods, in particular small-angle neutron scattering (SANS), are sensitive to structural organization features at a level of 1–100 nm.

Small angle scattering of X-rays (SAXS) and neutrons (SANS) is one of the most effective methods for studying structures with sizes from one to several hundred nanometers. The diffraction pattern is the result of interference of rays scattered elastically and coherently on the sample, that is, without changing the
wavelength and phase. The main advantage of small-angle scattering is the possibility of using it to study disordered objects and in the absence of the need for special sample preparation. The basic formulas that relate the scattering intensity to the structure of an object are determined only by the scattering power of the inhomogeneities and the contrast of their electron density with respect to the main matrix.\textsuperscript{15,14,16} Thus, small-angle scattering allows one to study objects of various physical nature and state of aggregation, including nanoparticles in an amorphous matrix (glass) or colloidal particles (quantum dots) in solution.\textsuperscript{17,18} Small-angle neutron scattering is generally applicable for studying the structure, shape (ball, ellipsoid, prism, cylinder, etc.), the ratio of the length and width of nanoparticles smaller than 100 nm in size.

When studying colloidal solutions by the small-angle neutron scattering, it should be taken into account that the irradiating neutrons from the reactor practically does not scatter on the nucleus of a hydrogen atom, but is absorbed by the hydrogen. Therefore, when using ordinary water as a solvent, the diffraction pattern is practically impossible to obtain. In addition to the proton, a neutron is present in the nucleus of a deuterium atom; therefore, neutrons from a reactor are scattered elastically on the deuterium nucleus. For this reason, to study the structure of colloidal solutions by small angle neutron scattering, heavy water D\textsubscript{2}O should be used as a solvent instead of ordinary H\textsubscript{2}O water. Indeed, coherent scattering amplitudes of hydrogen and deuterium atoms differ in magnitude and sign. This leads to the fact that the densities of coherent scattering amplitudes of light and heavy water also differ in magnitude and sign (~0.56 × 10\textsuperscript{-10} cm\textsuperscript{-2} and +6.39 × 10\textsuperscript{-10} cm\textsuperscript{-2}, respectively).\textsuperscript{19,20}

In small-angle neutron scattering, contrast variation plays an important role in studying the fine structure of nano-objects. The use of heavy water or a mixture of light and heavy water changes the scattering contrast between particles and solvent and allows us to study the heterogeneity of nano-objects.\textsuperscript{19,21} Measurements in heavy water can significantly reduce the concentration of the studied colloidal solutions compared to the concentration of colloidal solutions obtained using ordinary (light) water. Small-angle neutron scattering covers the wavelength range from 0.1 to 2.0 nm (1–20 Å), which corresponds to scattering vectors from 1 to 10\textsuperscript{-6} Å\textsuperscript{-1}.\textsuperscript{19} Such a wide range of scattering vectors allows the study of colloidal solutions with a very low concentration of nanoparticles.

To study colloidal solutions using small angle neutron scattering, it is most effective to use colloidal solutions obtained using heavy water. It is known that the solvent has a significant effect on the rate of chemical reactions, which is associated, in particular, with the dielectric constant of the solvent. The dielectric constant of ordinary H\textsubscript{2}O water and heavy D\textsubscript{2}O water at room temperature is ~81.0 and 78.2, respectively. Reactions involving D\textsubscript{2}O usually proceed at a slower rate than with H\textsubscript{2}O, and the solubility of salts in heavy water is slightly less (5–10\%) than in ordinary H\textsubscript{2}O.\textsuperscript{22} Recently, the difference between the standard reduction potentials of H\textsubscript{2}O and D\textsubscript{2}O during hydrothermal synthesis of iron-containing solids has been established.\textsuperscript{23} However, the effect of heavy water on the dissolution of salts has been studied very poorly, and the formation of sulfide colloidal solutions in heavy water has not been studied at all.

Nobody has obtained colloidal solutions of silver sulfide in heavy water, suitable for studying by small-angle neutron scattering. An essential property of these colloidal solutions should be their stability. In the literature there is no information about such colloidal solutions. From private reports it is known that attempts to synthesize stable colloidal solutions of silver sulfide in heavy water were failed. For example, stable colloidal solutions of Ag\textsubscript{2}S in ordinary water can be synthesized in solutions of silver nitrate AgNO\textsubscript{3}, sodium sulfide Na\textsubscript{2}S using 3-mercaptopropyl-trimethoxysilane (MPS) HSC\textsubscript{3}H\textsubscript{2}Si(OCH\textsubscript{3})\textsubscript{3} as a stabilizer.\textsuperscript{24} However, with the same synthesis in D\textsubscript{2}O heavy water using MPS, colloidal silver sulfide solutions are unstable: Ag\textsubscript{2}S nanoparticles precipitate 3–4 days after the synthesis of solutions.

Present work is devoted to study of the synthesis of stable colloidal solutions of silver sulfide in D\textsubscript{2}O heavy water as a solvent. Such research is carried out for the first time in the world. The main characteristics of Ag\textsubscript{2}S quantum dots synthesized in colloidal solutions of silver sulfide in heavy water are determined. Potentially synthesized colloidal solutions are intended for the subsequent study of the real fine structure of Ag\textsubscript{2}S quantum dots using small-angle neutron scattering. The study of fine structure is not available for other methods. Direct measurements of synthesized colloidal solutions by small-angle neutron scattering will be the subject of independent research.

2. Experimental

For the synthesis of colloidal solutions of Ag\textsubscript{2}S based on D\textsubscript{2}O, the same procedure was used as for the synthesis of colloidal solutions based on H\textsubscript{2}O described in study.\textsuperscript{25} Colloidal solutions of Ag\textsubscript{2}S were synthesized by chemical deposition from aqueous solutions of silver nitrate AgNO\textsubscript{3}, sodium sulfide Na\textsubscript{2}S and sodium citrate Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7} in high-purity deionized heavy water D\textsubscript{2}O. The D\textsubscript{2}O content in the used heavy water was not less than 99.9 mol\%, the admixture of light water H\textsubscript{2}O was less than 0.1 mol\%. The electrical conductivity of heavy water did not exceed 5 μS cm\textsuperscript{-1} = 0.0005 S m\textsuperscript{-1}.

A transparent stable colloidal solution with a solid dispersed phase of Ag\textsubscript{2}S (nano-Ag\textsubscript{2}S) was obtained by chemical deposition in D\textsubscript{2}O heavy water. Solutions of sodium sulfide Na\textsubscript{2}S and silver nitrate Ag(NO\textsubscript{3})\textsubscript{2} in heavy water with the same concentrations of 50 mmol L\textsuperscript{-1} were used as initial solutions. It was shown earlier\textsuperscript{26} that reaction mixtures with such concentrations are supersaturated with silver and sulfur ions; therefore, the synthesis of Ag\textsubscript{2}S was carried out for a very short time.

The synthesis was carried out at a temperature of 298 K in the dark. Sodium citrate in the synthesis of Ag\textsubscript{2}S in heavy water D\textsubscript{2}O plays the role of a stabilizing agent to prevent nanoparticle growth. The stabilizing role of sodium citrate in the hydrochemical synthesis of nanostructured silver sulfide in ordinary (light) water was described earlier in study.\textsuperscript{25,26} In colloidal solutions of Ag\textsubscript{2}S QDs in heavy water, citrate ions are attached on the surface of the Ag\textsubscript{2}S nanoparticles and form a negatively charged citrate layer, which prevents sulfide nanoparticles from coming together.
In aqueous solutions with low S\(^2-\) ion concentration, sodium citrate can reduce Ag\(^+\) ions to form silver metal nanoparticles\(^{26-28}\) and form a citrate shell on Ag\(_2\)S particles.\(^{29-33}\) Therefore, to obtain colloidal solutions of silver sulfide without Ag impurities and without a citrate shell, reaction mixtures with a small relative excess of sodium sulfide Na\(_2\)S and a minimum concentration of Na\(_3\)Cit were used. The synthesis was carried out in the dark in a neutral medium at pH ≈ 7 by the following reaction scheme

\[
2\text{AgNO}_3 + (1 + \delta)\text{Na}_2\text{S} \xrightarrow{\text{Na}_2\text{C}_6\text{H}_5\text{O}_7} \text{Ag}_2\text{S} \downarrow + 2\text{NaNO}_3, \tag{1}
\]

where 0.01 ≤ δ ≤ 0.5 is a small excess of Na\(_2\)S, needed for synthesizing Ag\(_2\)S colloidal solutions without admixture of Ag.

For the synthesis, solutions of Ag\(_2\)S, Na\(_2\)S, and Na\(_3\)Cit previously prepared in heavy water D\(_2\)O were used. The synthesis was performed in the following order: to 5 mL of a silver nitrate solution was poured in 5 mL of a sodium citrate (stabilizer) solution, and the resulting solution was mixed with 10 mL of a Na\(_2\)S solution for 1–2 seconds.

The stable colloidal solutions with Ag\(_2\)S quantum dots with an average size less than 20 nm were prepared from reaction mixtures 1–8 with silver nitrate concentrations \(C_{\text{AgNO}_3}\) from 0.3125 to 2.5 mmol L\(^{-1}\) (Table 1). Earlier, reaction mixtures of the same compositions were used for the synthesis of Ag\(_2\)S colloidal solutions in ordinary H\(_2\)O water.\(^{34}\) The identical reaction mixtures were used to compare the sizes of Ag\(_2\)S nanoparticles synthesized in aqueous colloidal solutions on heavy D\(_2\)O and ordinary H\(_2\)O water.

The size (hydrodynamic diameter \(D_{\text{DLS}}\) of Ag\(_2\)S quantum dots and the zeta potential \(\zeta\) were determined directly in the colloidal solutions by non-invasive Dynamic Light Scattering (DLS) method on a Zetasizer Nano ZS facility (Malvern Instruments Ltd.) at a temperature of 298 K. The He–Ne laser with radiation wavelength 633 nm was used as a radiation source, and the detection angle of backscattered light was 173°. To provide the reproducibility of results, the scattering of light and the size of particles was measured in each solution no less than three times. The conductivity of synthesized colloidal solutions was also determined on a Zetasizer Nano ZS instrument.

The synthesized colloidal solutions were dried by sublimation methods in an Alpha 1–2 LD plus freeze dryer (Martin Christ) at an ice condenser temperature of −55 °C (218 K). Dried powders of nanostructured silver sulfide stored in a Vacuum Desiccator Sanplatec MB, evacuated to a residual pressure of 13.3 Pa (0.1 mm Hg).

Dried silver sulfide powders were examined by X-ray diffraction (XRD) method on a Shimadzu XRD-7000 diffractometer in Cu K\(_\alpha1\) radiation. X-ray measurements were performed in the angle interval 2\(\theta\) = 20–95° with a step of \(\Delta(2\theta) = 0.02°\) and scanning time 20 s in each point. The determination of the crystal lattice parameters and final refinement of the structure of the synthesized sulfide powders were carried out with the use of the X’Pert Plus software suite.\(^{34}\)

The JEOL JEM-2010 transmission electron microscope with 0.14 nm (1.4 Å) lattice resolution was also used to determine the size of Ag\(_2\)S quantum dots. The elemental chemical composition of Ag\(_2\)S quantum dots was studied on the same microscope with the use of an Phoenix (EDAX) Energy Dispersive Spectrometer with a Si(Li) detector having energy resolution of 130 eV. Colloidal solutions of Ag\(_2\)S quantum dots were placed on a copper grid for examination. A copper grid with an aperture diameter of 50 μm was used for TEM observing of nanoparticles. Additionally, one or two layers of hydrocarbon-glue were applied to copper grid.

In addition, the average particle size \(D\) (to be more precise, the average size of coherent scattering regions (CSR)) in synthesized dried silver sulfide nanopowders was estimated by XRD method from the diffraction reflection broadening using the dependence of reduced reflection broadening \(\beta_s(2\theta) = \sqrt{\delta(2\theta)\cos\theta}/\lambda\) on the scattering vector \(s = (2 \sin \theta)/\lambda.\(^{35}\)

UV–vis absorption spectra of colloidal solutions of Ag\(_2\)S QDs were recorded on a Shimadzu UV-2401 PC spectrophotometer at room temperature.

The photoluminescence (PL) emission spectra of quantum dots were measured under an excitation of 658 nm on a spec- photrometer FLS920 (Edinburgh Instrument).

### 3. Discussion

The XRD pattern of silver sulfide nanopowder obtained by sublimation drying of colloidal solution 6 in heavy water D\(_2\)O (Table 1) is shown in Fig. 1a. The diffraction reflections of the

| No. | AgNO\(_3\) (mmol L\(^{-1}\)) | Na\(_2\)S (mmol L\(^{-1}\)) | Na\(_3\)Cit (mmol L\(^{-1}\)) | \(D_{\text{DLS}} \pm 0.5^a\) (nm) | \(D_{\text{DLS}} \pm 0.5^b\) (nm) | \(D_{\text{TEM}}\) (nm) \(^{25}\) | \(D_{\text{DLS}} \pm 0.5^a\) (nm) | \(D_{\text{TEM}}\) (nm) \(^{25}\) |
|-----|----------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1   | 0.3125         | 0.165          | 5              | 3.1             | 3.5             | 2–3             | 2.3             | 2–3             |
| 2   | 0.3125         | 0.168          | 2.5            | 4.2             | 5.1             | 3–5             | 2.7             | 2–3             |
| 3   | 0.3125         | 0.170          | 1              | 6.5             | 7.9             | 6–7             | 3.1             | 4–7             |
| 4   | 0.625          | 0.313          | 5              | 8.7             | 10.1            | 8–9             | 4.2             | 3–4             |
| 5   | 0.625          | 0.325          | 3.75           | 10.1            | 10.7            | 8–10            | 5.6             | 5–6             |
| 6   | 2.5            | 1.30           | 1              | 11.7            | 14.2            | 10–12           | 8.0             | 8–10            |
| 7   | 0.625          | 0.330          | 2.5            | 15.7            | 17.3            | 15–16           | 9.2             | 8–10            |
| 8   | 0.625          | 0.335          | 1.25           | 18.7            | 20.0            | 18–20           | 10.0            | 9–11            |

\(^a\) Quantum dot size corresponding to the maximum of \(D_{\text{DLS}}\) size distribution. \(^b\) The average quantum dot size according to DLS data.
The size of Ag$_2$S quantum dots in colloidal solutions varies from 0.067 to 0.108 S m$^{-1}$. An increase in the conductivity of colloidal solutions in comparison with the heavy D$_2$O water used confirms the presence of quantum dots with electric charges in solutions. Thus, silver sulfide colloidal solutions synthesized using D$_2$O heavy water retained the stability and unchanged QDs size after storage for more than 100 days, i.e., they have the same high stability as colloidal solutions synthesized in ordinary H$_2$O water.

Transmission electron microscopy (TEM) confirmed the small size of the Ag$_2$S quantum dots in the synthesized colloidal solutions.

A TEM image of quantum dots contained in a colloidal solution obtained from reaction mixture 3 with a minimum concentration of sodium citrate is shown in Fig. 3. The size of nanocrystalline silver sulfide with a monoclinic (space group P2$_1$/c) structure of Ag$_{1.93}$S acanthite obtained from colloidal solution 6 in D$_2$O heavy water (Table 1). For comparison, an XRD pattern of a larger nanopowder of monoclinic silver sulfide with a particle size of ~40–45 nm is shown.

According to DLS data, the average size of Ag$_2$S quantum dots in colloidal solutions no. 1–8 does not exceed 20 nm (Fig. 2). The quantum dot size corresponding to the maxima of the size distributions $D_{	ext{DLS}}$ is from 2 to 10 nm (Table 1), and the average quantum dot size $D_{\text{DLS}}$ in the obtained colloidal solutions varies from ~3 to ~11 nm. With an increase in the concentration of silver nitrate in the initial reaction mixtures, the size of Ag$_2$S quantum dots in the synthesized colloidal solutions increases slightly. A decrease in the concentration of sodium citrate, all other things being equal, leads to a decrease in the stabilizing effect of Na$_3$Cit and is also accompanied by some increase in the size of Ag$_2$S quantum dots (Table 1).

The size distributions of Ag$_2$S quantum dots in synthesized colloidal solutions, measured by the DLS method, are shown in Fig. 2.
most quantum dots is from 6 to 7 nm. This is consistent with measurements of the size distribution of Ag2S quantum dots in this solution by dynamic light scattering (see Fig. 2). As an example, HRTEM image of a quantum dot about 6 nm in size is shown in Fig. 3a. The selected area of electron diffraction (Fig. 3b) was calculated using the Fast Fourier Transform (FFT) of HRTEM image of this quantum dot. A detailed description of the Fast Fourier Transform using the Gatan Microscopy Suite program37 is given on the site.42 The observed electron diffraction spots (011) and (102) correspond to the [21 −1] plane of the reciprocal lattice of monoclinic (space group P21/c) silver sulfide with α-Ag2S acanthite structure. To reliably identify the observed diffraction reflections and their indices, it is necessary to calculate the angle \( \varphi_{\text{diff}} \) between the reflections with the expected indices \((h,k,l)\) on the selected area of electron diffraction, i.e., the angle between the lines passing through each reflection and the central spot (000). The coincidence of the estimated and experimental \( \varphi_{\text{diff}} \) angles unequivocally proves that the indices \((h,k,l)\) are determined correctly. According to study,42 the formula for determining the \( \varphi_{\text{diff}} \) angle between the reflections \((h_1,k_1,l_1)_{\text{mon}}\) and \((h_2,k_2,l_2)_{\text{mon}}\) in the reciprocal lattice of the monoclinic structure has the form

\[
\cos \phi = \frac{h_1h_2/a^2 + k_1k_2/b^2 + 1 \cdot (h_1l_2 + h_2l_1)ac \cos \beta + h_1h_2c^2 \cos^2 \beta}{d_i \times d_j},
\]

where \(d_i = \sqrt{(h_i/a)^2 + (k_i/b)^2 + [(l_ia - h_ic \cos \beta)/(ac \sin \beta)]^2}\) with \(i = 1 \text{ or } 2\).

In Fig. 3b, the angle between the supposed reflections (011) and (−102) is \(76.4^\circ\). The calculated angle between reflections with such indices for monoclinic silver sulfide should be 76.4° and coincides with the observed angle. Consequently, the reflection indices are defined correctly. The analysis has shown that these reflections are observed along the [2−11] zone axis.

Analysis of the HRTEM image (Fig. 3) confirmed that, as a result of synthesis in colloidal solutions in heavy water, monoclinic (space group P21/c) silver sulfide with α-Ag2S acanthite structure is actually formed. Fig. 4 show TEM images of colloidal solutions 4 and 5. It is seen that the size of silver sulfide quantum dots in colloidal solution 4 is from 8 to 9 nm (Fig. 4a). According to TEM, the size of silver sulfide quantum dots in colloidal solution 8–10 nm (Fig. 4b).

Larger silver sulfide quantum dots are observed in colloidal solution 6: the Ag2S quantum dot from this solution has a size of \(\sim 12\) nm (Fig. 5). Fig. 5 clearly shows the interplanar distance 0.187 nm, which coincides with the distance between the atomic planes (014) of silver sulfide with monoclinic (space group P21/c) structure of the α-Ag2S acanthite type.37,43,44 The inset shows the EDX spectrum of Ag2S nanoparticles from colloidal solution 6.
TEM images of colloidal solutions, as well as the sizes of quantum dots according to TEM which given in Table 1, confirm the results of DLS measurements of quantum dot size.

In the EDX spectra obtained using a JEOL JEM-2100 transmission electron microscope, in addition to silver and sulfur, Kz lines of copper Cu from the copper grid are observed, on which the quantum dots under study and a weak Kz line of carbon C from the glue were applied (see Fig. 5, inset). A source of carbon C in colloidal solutions of silver sulfide is also an admixture of the initial reagent – sodium citrate Na3Cit. The sodium citrate solution is adsorbed on the surface of Ag2S quantum dots. According to EDX data, impurity oxygen is also present in silver sulfide quantum dots, which is distributed over the surface of the particles, which is reflected in the presence of a weak Kz line of oxygen at 0.525 keV.

According to the EDX results (Fig. 5, inset), minus the impurity elements, the silver and sulfur contents in the synthesized silver sulfide are 83.4 ± 0.5 and 12.8 ± 0.2 wt%, which corresponds to silver sulfide Ag1.96±0.02S1.00±0.01.

The UV-vis absorption spectra of colloidal solutions 1–8 are displayed in Fig. 6. According to the DLS data, the size of Ag2S QDs in these solutions changes from 3.1 to 18.7 nm. The UV-vis absorption spectra of the investigated colloidal solutions reveal wide bands (Fig. 6) characteristic of semiconductor QDs in the region from 280 to 800 nm (4.40–1.55 eV) associated with the ground state exciton absorption.

The weak absorption peak observed at ~280–310 nm corresponds to Ag2S nanoparticles.45,46 This weak absorption peak is absent in the absorption spectra of Ag2S QDs with a size more than 8.7 nm. Considering a large experimental data array,47–49 the absorption spectra of colloidal Ag2S QDs do not contain a peak corresponding to the ground state exciton absorption. It can be assumed that the considerable contribution to the absorption band of colloidal QDs is associated with the nonstoichiometry of silver sulfide,50 which is always accompanied by impurity absorption and leads to the absence of features in the absorption spectrum.

The position of the ground state exciton absorption band in the UV-vis absorption spectra of colloidal solutions 1–5 was found from the minimum of the second derivative for the optical absorption spectra with respect to the photon energy. These positions are marked by arrows in Fig. 6.

Fig. 7 presents the size-dependent photoluminescence (PL) emission spectra of Ag2S colloidal solutions 1–5 in which the fluorescence of Ag2S quantum dots is tunable from ~1090 to ~1182 nm by increasing the nanoparticle size Ddls from 3.1 to 10.1 nm. PL emission spectra of colloidal solutions 5, 6, 7, and 8 with Ag2S quantum dots larger 8 nm practically coincide; therefore, only the spectrum of colloidal solution 5 is shown in Fig. 7.

According to,50 the PL peak for Ag2S quantum dot with a size about 1.5 nm is observed at a wavelength of ~640 nm (see Fig. 7); the PL emission spectrum of Ag2S QD with a size about 1.5 nm was measured under an excitation of 785 nm. Perhaps,
there was a misprint in study58 because generally the PL emission wavelength of the sample is longer than it’s the excitation wavelength. In study58 water-soluble Ag2S quantum dots have been synthesized at heating of mixed solution of mercapto-
-propionic acid, ethylene glycol, and silver nitrate AgNO3. The PL emission peaks shift from ~1090 to ~1182 nm with the size of Ag2S quantum dots increasing from ~3.1 to 10.1 nm and keep constant at 1182–1190 nm with increase of the quantum dot size from ~10.1 to 16 nm and further. The continuous blue shift of the PL emission of Ag2S quantum dots from ~1182 to ~640 nm may be attributed to the strengthened quantum confinement effect and increasing the band gap Eg which resulted from the decreasing Ag2S quantum dots size (band gap of bulk monoclinic Ag2S crystals is about 1.0 eV).25,51 Almost constant position of the PL emission peaks at ~1140–1180 nm for the Ag2S quantum dots with a boundary value of size 4.2 nm and larger is evidence for transition from the strong quantum confinement regime to the weak quantum confinement regime. The absence of quantum confinement for semiconductor Ag2S nanocrystals larger 4 nm is in good agreement with the data.51–53 Thus, we experimentally estimated Ag2S exciton radius Rex as less than half of boundary value of size 4.2 nm, i.e. ≤2.1 nm.

According to,54 the characteristic size of the Wannier–Mott exciton (or the Bohr radius of the of the first exciton state) in the macroscopic semiconductor is determined by the equation

$$\text{Rex} = \frac{\hbar^2 \epsilon}{2 \epsilon m_e} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) = \frac{\hbar^2 \epsilon}{\mu_{ex} \epsilon^2}, \quad \text{(3)}$$

where \(\hbar = 1.055 \times 10^{-27} \text{ cm}^2 \text{ g s}^{-1}\) is the reduced Planck constant, \(\epsilon = 4.803 \times 10^{-10} \text{ cm}^{1/2} \text{ g}^{1/2} \text{ s}^{-1}\) is the charge on the electron, \(\mu_{ex} = m_e m_h/(m_e + m_h)\) is the reduced exciton mass, and \(m_e\) and \(m_h\) are the electron and hole effective masses. For Ag2S, dielectric constant \(\epsilon\) is about 6, \(m_e = 0.286 m_0\) and \(m_h = 1.096 m_0\) \((m_0 = 9.1095 \times 10^{-28} \text{ g}\) is the free electron mass),55 respectively. Taking this into account, the reduced exciton mass \(\mu_{ex}\) for acanthite \(\alpha\)-Ag2S is equal ~0.23\(m_0\). At such values of \(\epsilon, m_e\) and \(m_h\), the Ag2S exciton radius \(\text{Rex}\) which is calculated by the formula (3) is equal to ~1.4 ± 0.1 nm, and the exciton diameter is 2.8 mm. However in study55 there are no data on the Brillouin zones estimation or measurement of effective masses by cyclotron resonance. Other effective masses of carriers are given in study55 \(m_e = 0.42 m_0\) and \(m_h = 0.81 m_0\). These effective masses of electron and hole have been calculated for the lowest conduction band and the highest valence band centered at \(\Gamma\) point of the Brillouin zone of Ag2S, respectively. Apparently, results of study55 on the electron and hole effective masses are more correct. According to,56 real part of dielectric constant \(\epsilon\) of silver sulfide is equal to 8.36. For these values \(m_e, m_h\) and \(\epsilon\) exciton mass \(\mu_{ex}\) is ~0.28\(m_0\), exciton radius \(\text{Rex}\) is equal to ~1.6 ± 0.1 nm, and the exciton diameter is ~3.2 nm.

Found exciton diameter ~3 ± 0.2 nm of silver sulfide is in satisfactory agreement with experimentally estimated Ag2S exciton diameter ~4.2 nm which follows from the size-dependent PL emission spectra (see Fig. 7).

Photoluminescence bands of Ag2S colloidal solutions 1–5 (Fig. 7) are distinguished by the significant Stokes shift of luminescence peaks relative to the position of ground state exciton absorption (see Fig. 6), which increases slightly with decreasing the QD size. The Stokes shift values lie at 0.93–0.99 eV. Fig. 8 shows the change in energies corresponding to the luminescence peaks of colloidal solutions 1–8, depending on the size (diameter) of the Ag2S QDs. It is clearly illustrated that there is no obvious blue shift of either excitonic energy until the size of QDs is below ~5 nm. As the QD size \(D \to \infty\) increases, the deviation of the excitonic ground state energy from the band gap value of bulk Ag2S allows one to estimate the exciton binding energy. According to the estimate, it is about 0.05 eV. This is quite close to the exciton binding energy value found in study55 and equal to 0.096 eV.

4. Conclusion

For the first time, colloidal solutions of silver sulfide quantum dots were synthesized in heavy water D2O. The synthesized colloidal solutions retain stability and small size of the quantum dots during long-term storage for more than 100 days. The high stability of colloidal solutions synthesized in heavy water is confirmed also by the large negative value of their zeta potential.

Sodium citrate in the synthesis of Ag2S in heavy water D2O plays the role of a stabilizing agent. In colloidal solutions of Ag2S QDs in heavy water, citrate ions are attached on the surface of the Ag2S QDs and form a negatively charged citrate layer, which prevents sulfide quantum dots from coming together.

The study of colloidal solutions of silver sulfide synthesized in D2O heavy water by dynamic light scattering, transmission electron microscopy, and X-ray energy dispersive analysis has shown that under these synthesis conditions it was possible to obtain colloidal solutions with silver sulfide QDs from 3 to 19 nm in size with monoclinic (space group \(P2_1/c\)) \(\alpha\)-Ag2S acanthite structure. Changing the concentration of reagents in the reaction mixtures allows us to control the size of silver sulfide QDs in the resulting colloidal solutions in the range from 2–3 to 20 nm.
An increase in the concentration of silver nitrate and a decrease in the concentration of sodium citrate in the initial reaction mixtures lead to a small increase in the size of Ag$_2$S QDs in the synthesized colloidal solutions no. 1–5. The size of Ag$_2$S quantum dots in colloidal solutions synthesized in D$_2$O heavy water is slightly (by 1–2 nm) larger than in colloidal solutions in ordinary H$_2$O water. This is evidence of the specific synthesis and stabilization of colloidal particles of silver sulfide in heavy water compared to ordinary water. It can be assumed that the difference in the size of the quantum dots is associated with different properties of the dispersed medium (heavy and ordinary water), in particular, with a lower solubility of sodium citrate in heavy water compared to ordinary water that leads to a slight weakening of the stabilizing effect of sodium citrate.

The prepared colloidal solutions are suitable for studying the structure of silver sulfide quantum dots by the method of small-angle neutron scattering.

Author contributions
Stanislav I. Sadovnikov: ideas and formulation of research aims, methodology, synthesis and investigations, validation, writing – review and editing, supervision. Aleksandr I. Gusev: analysis of the data, writing – original draft, project administration.

Conflicts of interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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