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Preparation of inks based on colloidal AgInS₂ nanocrystals and their application in microplotter printing of photosensitive structures

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For the first time, ligand exchange in solution was used to produce inks based on colloidal AgInS₂ nanocrystals that are suitable for the fabrication of photosensitive structures. Within this study, a system of stabilizing ligands was identified that allowed the resulting sol in dimethylformamide to remain stable for two weeks without significant agglomeration. FTIR spectroscopy confirmed the completeness of the ligand exchange. Using a microplotter, a photosensitive, photoconductive-type structure was fabricated on gold interdigitated electrodes from the obtained colloidal materials, and its photoelectrical characteristics were measured under illumination with a 405 nm laser.

Keywords: silver indium sulfide, hot injection synthesis, nanocrystals, colloidal quantum dots, thin films.

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Introduction

Colloidal quantum dots represent a new class of nanomaterials with the possibility of modifying optical properties through the modification of semiconductor nanoparticle sizes [1, 2]. The synthesis of colloidal nanocrystals is typically carried out by hot injection synthesis using long-chain surfactants that act as ligands and stabilizers of the forming nanoparticles. These organic ligands make it possible to obtain nanocrystals with a narrow size distribution and a low-defect surface. Furthermore, they ensure the long-term sedimentation stability of the resulting sols. Unfortunately, these same long-chain ligands act as insulators and do not allow thin layers of colloidal nanocrystals with good conductivity to be obtained. Therefore, to create thin photosensitive conductive films based on colloidal quantum dots (CQDs), the method of

layer-by-layer deposition with in-situ ligand exchange is typically used. The replacement of long-chain ligands with short-chain ones directly within the films makes it possible to ensure conductivity while preserving the individuality of the deposited nanoparticles. Thus, both photoresistors and more complex multilayer structures, such as photodiodes, can be obtained. The weak point of this method is the difficulty of obtaining relatively thick films, since the rate of ligand exchange in the film drops sharply with increasing thickness. Also, many exchange reactions occurring during heterophase processing do not allow a high percentage of original ligand replacement to be achieved even in thin films with the thickness of a nanocrystal monolayer (i.e., 5–10 nm) [3, 4]. In recent years, as an alternative approach for obtaining conductive films based on colloidal nanocrystals, the replacement of long-chain ligands in solution

to produce relatively stable colloidal solutions of nanocrystals with short-chain ligands has been proposed [5]. In these colloids, sedimentation stability is typically ensured by electrostatic stabilization [6]. Colloidal solutions of this type make it possible to create thin films possessing photosensitivity and conductivity directly, without additional ligand exchange steps in the films. The deposition can be carried out by spin-coating or by aerosol printing methods. From the point of view of obtaining photosensitive structures, printing is the most attractive method, as it allows for reduced consumption of nanomaterials and precise deposition in selected areas [7].

Monitors and televisions manufactured using quantum dot light-emitting diode (QLED) technology are widely available in electronics chain supermarkets today. Cadmium selenide (CdSe) colloidal quantum dots (CQDs) used in QLED technology as phosphor materials are synthesized according to well-developed and reproducible methods. However, despite the technological advantages, this system has a serious drawback – the environmental toxicity of cadmium compounds. The use of cadmium not only creates additional production safety requirements but also increases the risk of environmental pollution in case of device damage, disposal, or improper recycling. It is this factor that is one of the important constraining factors for the proliferation of solar cells based on cadmium chalcogenide nanocrystals. These environmental limitations stimulate the search for alternative materials and the development of safer technologies [8, 9].

Colloidal nanocrystals of ternary chalcogenides of the ABX_2 type represent a promising class of semiconductor nanomaterials for applications in solar cells, flexible displays, and photosensors [10]. Silver indium disulfide ($AgInS_2$) has a band gap estimated to be 1.87 eV for the bulk material and exciton Bohr radius of 5.5 nm. Thus, as a nanomaterial, it is of interest as a possible alternative to CdSe.

Conductive thin films based on $AgInS_2$ nanocrystals have been obtained by a number of methods, including the layer-by-layer deposition method with exchange for mercaptopropionic acid [11]. Direct deposition methods for $AgInS_2$ sols are poorly studied and are of little suitability for creating photosensitive structures. A previously published study on the creation of a

solar cell based on a colloidal $AgInS_2$ solution, designated by the authors as an "ink", also includes annealing of the obtained films at 450 °C in an atmosphere of elemental sulfur [12]. In addition, drop-casting was used as the deposition method, rather than any type of printing. The creation of inks based on $AgInS_2$ nanocrystals with a ZnS shell for creating luminescent labels has been recently published [13]. This system contains stabilizing long-chain ligands, as well as polymethyl methacrylate, which precludes its application in the creation of sensor or photosensitive structures.

To date, we have been unable to find examples in the literature of obtaining inks, i.e., sols of $AgInS_2$ colloidal quantum dots with ligands that allow the creation of thin films with good conductivity. Such "inks" have been developed for a number of nanocrystals of binary chalcogenides, such as PbS [14, 15], CdSe [16], PbSe [17], and HgTe [18]. Within the framework of the presented work, a system suitable for obtaining "inks" based on $AgInS_2$ was found for the first time, and photosensitive resistive-type elements were fabricated using a microplotter.

Materials and methods

Reagents

The following chemicals were used in the synthesis of $AgInS_2$ CQDs without further purification: indium iodide (99 %, Lanhit), sulfur (99.99999 %, Reakhim), 1-decene (90 %, Vekton), 1-dodecanethiol (Acros, 99 %), 2-mercaptoethanol (95 %, Vekton), n-butylamine (95 %, Vekton), silver nitrate (chemically pure, Vekton), hexane (99 % HPLC grade, Macron Fine Chemicals), decane (ultra-high purity, Komponent-Reaktiv), oleic acid (90 %, Vekton), and oleylamine (80–90 %, Acros), which was dried by heating (100 °C) under reduced pressure (1 mbar). Indium stearate was prepared from metallic indium according to the method described in the literature [19]. Silver stearate was synthesized from silver nitrate [20].

Measurement methods

The size, morphology, and structure of the nanoparticles were studied using a JEM-2100 transmission electron microscope (TEM) by JEOL (Japan) at an accelerating voltage of 200 kV. The crystal structure was analyzed by comparing the interplanar distances measured

from the obtained selected area electron diffraction (SAED) images to the values from the database of crystal structures. The optical properties were evaluated by spectrophotometry methods using a JASCO V-770 spectrophotometer (JASCO) and by infrared spectrometry using a Spectrum 100 FTIR spectrometer (PerkinElmer) equipped with a multiple attenuated total internal reflection (MATIR) attachment containing Ge and ZnSe prisms (incidence angle 45° , number of reflections 25). Electrical characteristics were measured using a Keithley 4200A-SCS source measurement unit under illumination from a 405 nm laser. The surface morphology of the thin films was studied using NT-MDT Solver-PRO atomic force microscope in tapping mode.

Obtaining the sulfur precursor

A total of 15.625 mmol (0.5 g) of elemental sulfur was dissolved in 10 mL of 1-decene at a temperature of 185°C and elevated pressure in a screw-cap thick-walled tube for 1 hour. The resulting dark yellow solution was used as a sulfur precursor in the synthesis of nanocrystals.

Synthesis procedure for AgInS_2 CQDs

Silver nitrate (10.2 mg, 0.06 mmol) and indium stearate (57.9 mg, 0.06 mmol) were added to a mixture of 0.4 mL of oleic acid, 0.3 mL of 1-decene, and 3 mL of decane. The resulting mixture was heated under an argon flow at 110°C until a homogeneous solution formed. The resulting solution was diluted with 27 mL of decane and heated to 150°C . The sulfur solution in 1-decene (1.56 M, 1.5 mL) was injected at 150°C . The reaction mixture acquired a brown color during the reaction, and the temperature was maintained at 150°C . After 60 min, the flask was immersed in an ice bath. AgInS_2 nanoparticles were isolated by double reprecipitation. Isolation and purification of the CQDs were carried out by adding a 1:2 methanol:isopropanol mixture followed by centrifugation and redispersion in n-hexane (1.5 mL of the alcohol mixture per 2.5 mL of the reaction mixture for the first precipitation, and 0.6 mL of the alcohol mixture per 1 mL of CQDs in n-hexane for the second precipitation). The nanocrystals were redispersed in n-hexane.

Procedure for preparing AgInS_2 CQD inks

Sodium acetate (8.2 mg, 0.1 mmol) was added to a solution of indium iodide in

dimethylformamide (0.1 M, 2 mL) under argon and dissolved with stirring. A volume of 0.2 mL of 2-mercaptoethanol was added to the resulting solution to form a homogeneous solution. This solution was mixed with an AgInS_2 CQD sol in n-octane, with an interface between the hydrophilic and hydrophobic phases being observed. The resulting mixture was stirred for 20 minutes, after which the AgInS_2 CQDs transferred from the hydrophobic phase to the hydrophilic phase. The CQDs with a hydrophilic ligand shell were isolated by centrifugation of the mixture for 10 minutes at 3000 rpm in the form of a dark precipitate. The resulting finely crystalline precipitate was redispersed in 2 mL of DMF with the addition of 0.2 mL of n-butylamine. Then, the product was isolated by single reprecipitation by adding tetrachloroethylene (3 mL of TCE per 1 mL of sol in DMF) followed by centrifugation and redispersion in DMF.

Procedure for fabricating a photoresistor based on AgInS_2 CQD inks by the drop-casting method

A volume of 50 μL of the AgInS_2 CQD solution in dimethylformamide was dropped onto a substrate that had been pre-cleaned from resist using hot (90°C) n-methylpyrrolidone and rinsed in boiling isopropanol. For more complete evaporation of DMF, the substrate was placed on a hotplate at 70°C .

Findings and Discussion

Colloidal nanocrystals obtained with a sulfur precursor based on 1-decene were chosen as possible precursors for inks based on AgInS_2 nanoparticles [21].

The synthesis of colloidal AgInS_2 nanoparticles was carried out according to a modified procedure developed earlier. AgNO_3 was used instead of silver stearate as the silver precursor [22]. The synthesis was carried out at 150°C in decane as the solvent. This procedure allows nanocrystals to be obtained with a ligand shell consisting of oleic acid and oleylamine, which makes it possible to replace the original shell with different types of short-chain ligands. The obtained nanocrystals possess a chalcopyrite crystal structure and exhibit absorption in the visible range (Fig. 1). The as-synthesized AgInS_2 nanomaterial has an absorption edge at 700 nm and an excitonic peak maximum at about 580 nm.

TEM micrographs showed that the nanocrystals have the rectangular shapes, including rectangular morphologies with protrusions on one face, and exhibit an average

size of about 16 nm (Fig. 2a–b). Analysis of the size distribution histograms showed that the distribution is relatively narrow with a standard deviation of to 3.98.

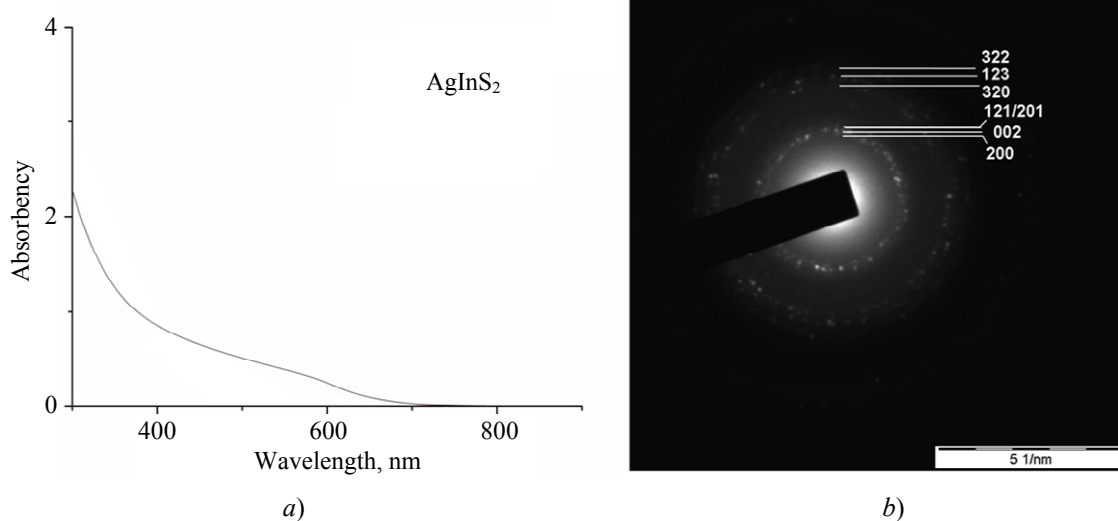


Fig. 1. AgInS₂ CQDs a) Absorption spectrum (visible range, 300–700 nm); b) SAED image

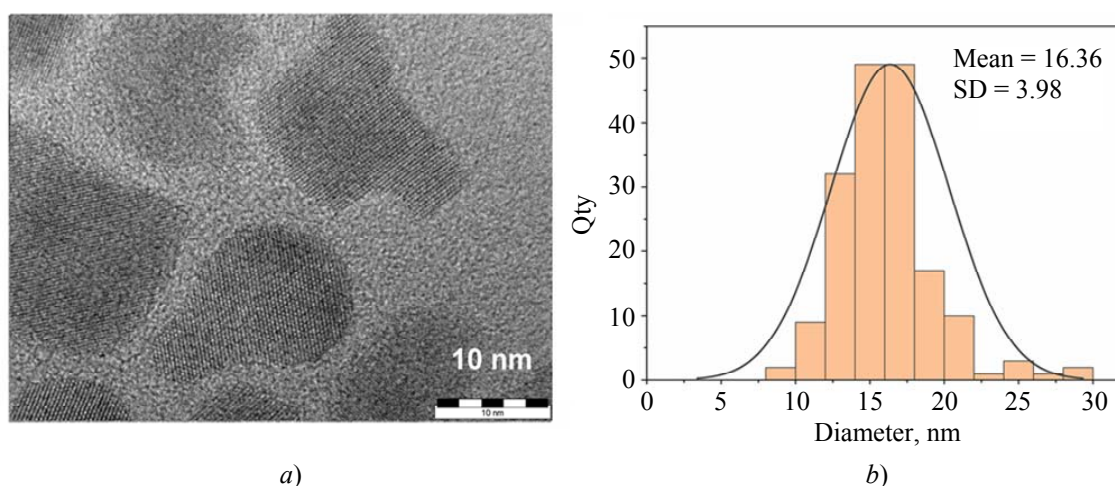


Fig. 2. a) TEM image and b) size distribution diagram AgInS₂ CQDs

To prepare inks from nanocrystals of binary chalcogenides, such as PbS, CdSe, or HgTe, the original ligand shell is usually replaced in dimethylformamide with the halide of the corresponding metal and butylamine. The substitution is usually carried out in a two-phase system, and the efficiency of the ligand exchange can be judged by the transfer of nanoparticles from one phase to another accompanied by a change in their color. For the hydrophobic phase, this corresponds to a change in color from black to colorless, and for the hydrophilic dimethylformamide phase, from colorless to colored.

As already mentioned, the preparation of inks based on colloidal AgInS₂ nanocrystals has not been previously described in the literature. In this case, by analogy, either silver halides, or indium halides, or a mixture of both metal salts, can be used. Initial experiments showed that the use of silver halides or mixtures with them for carrying out the substitution is difficult due to their extremely low solubility. Thus, systems based on indium halides were chosen for optimization. Substitution of the original ligand shell with a phase transfer was observed when using indium iodide for the studied nanocrystals with a carboxylate shell. At the same time, the

resulting colloidal solutions exhibited very low stability and degraded almost instantly with the precipitation of AgInS_2 nanoparticles, which could not be redispersed back into a stable sol.

For using nanocrystal sols as inks, the key factor is sedimentation stability. The authors achieved long-term colloidal stability using a combination of *n*-butylamine and 2-mercaptoethanol based on AgInS_2 nanocrystals. At the same time, the resulting AgInS_2 sols in DMF did not precipitate upon the addition of toluene, as described for analogous sols, which complicated their purification and isolation. The use of tetrachloroethylene as a nonsolvent solved this problem.

TEM investigation showed that the nanocrystals after ligand substitution retain a size close to the original, while acquiring a more spherical shape. SAED showed the retention of the chalcopyrite crystal structure of AgInS_2 .

At the same time, the crystallinity of the sample increases; furthermore, the relative intensity of the reflection from the 122/202 plane increases.

A comparative study of films obtained from the original colloidal AgInS_2 nanocrystals and AgInS_2 "inks" in dimethylformamide showed that the signals of the original shell consisting of long-chain carboxylate ligands disappear. Thus, the intensity of the signals of stretching vibrations of methylene groups at 2950 cm^{-1} drops fivefold as a result of the substitution of oleate with butylamine, and the signal of the carboxylate ion at 1585 cm^{-1} completely disappears. At the same time, a signal of the carbonyl group of dimethylformamide coordinated on the surface of the nanocrystals appears at 1661 cm^{-1} . Also, a broad peak with a maximum at 4050 cm^{-1} , associated with an intraband transition, appears in the IR region.

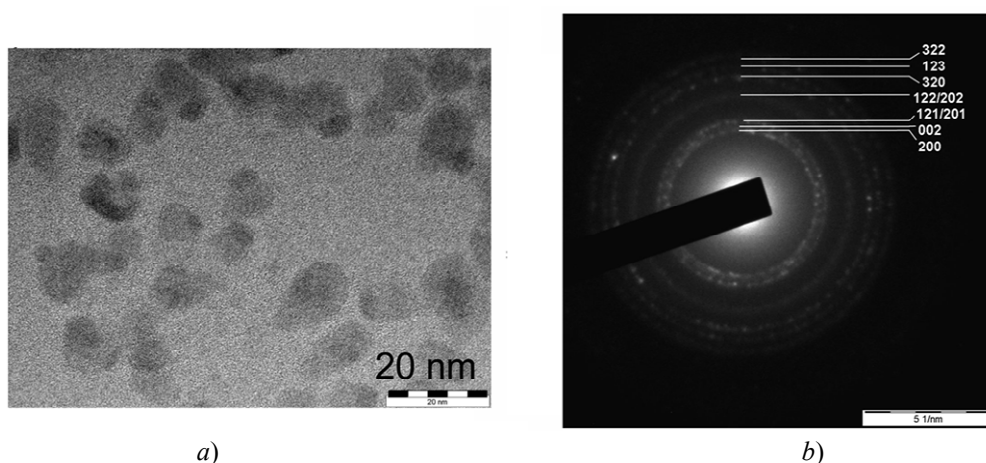


Fig. 3. AgInS_2 CQD "inks" a) TEM image and b) SAED

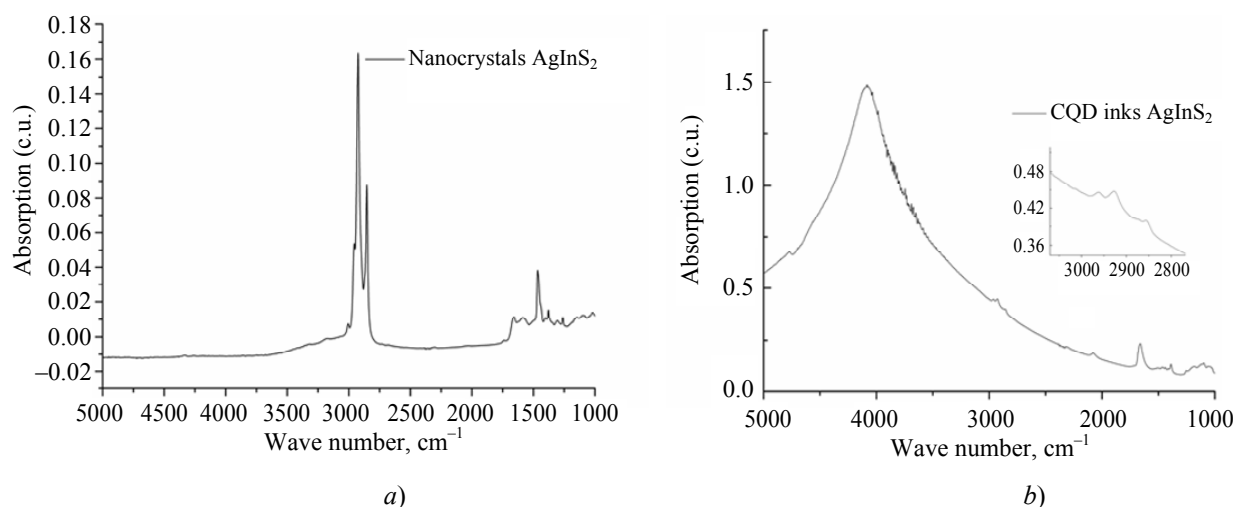


Fig. 4. a) IR spectra in the range of $5000\text{--}1000\text{ cm}^{-1}$; b) AgInS_2 CQD nanoparticles before ligand exchange in solution and after ligand exchange

The process of forming thin-film functional conductive microstructures was performed using a SonoPlot GIX Microplotter II (SonoPlot, Middleton, WI, USA). The microplotter allows the use of picoliter volumes of liquid for depositing functional elements with planar dimensions down to 5 μm . Deposition occurs using a liquid ejection technology via a nozzle that employs ultrasonic vibration generated by a piezoelectric element. In this case, the capillary positioning accuracy reaches 5 μm . A wide range of liquids can be used with this microplotter: the viscosity of functional inks can reach 450 cP, which significantly exceeds similar characteristics of typical inkjet printers operating on the drop-on-demand principle. The formation of elements was carried out using CQD-based inks on silicon oxide substrates with an oxide thickness of 260 nm and gold electrodes prefabricated by lithography. Two types of substrates were fabricated with the following electrode geometries: interdigitated electrodes with gaps between electrodes of 2, 3, and 5 μm , and "bow-tie" electrodes with gaps between electrodes of 30, 20, and 10 μm .

A glass capillary with a nozzle diameter of about 400 μm was chosen for printing. Before printing, the capillary was filled with ink and lowered to a distance of 5–10 μm above the substrate, and a control voltage of 10 V was applied to the piezoelectric element to form contact between the ink and the substrate, after which the control voltage was reduced to 1 V. During the printing process, the capillary moved at a speed of 10 mm/s, and the control voltage applied to the piezoelectric element remained unchanged. Printing was carried out in one and two layers for the interdigitated electrodes, and in one, two, and four layers for the "bow-tie" electrodes. After printing, the samples were dried at room temperature.

Surface investigation using AFM showed a high degree of surface uniformity of the obtained thin-film samples (Fig. 5).

The obtained photoresistor samples showed an increase in conductivity under the action of monochromatic radiation with a wavelength of 405 nm. The maximum photocurrent value at an incident radiation power density of 0.9 mW/mm² was 0.18 pA, with a dark current of 0.01 pA (Fig. 6), which provides a sensitivity of 0.03 $\mu\text{A/W}$.

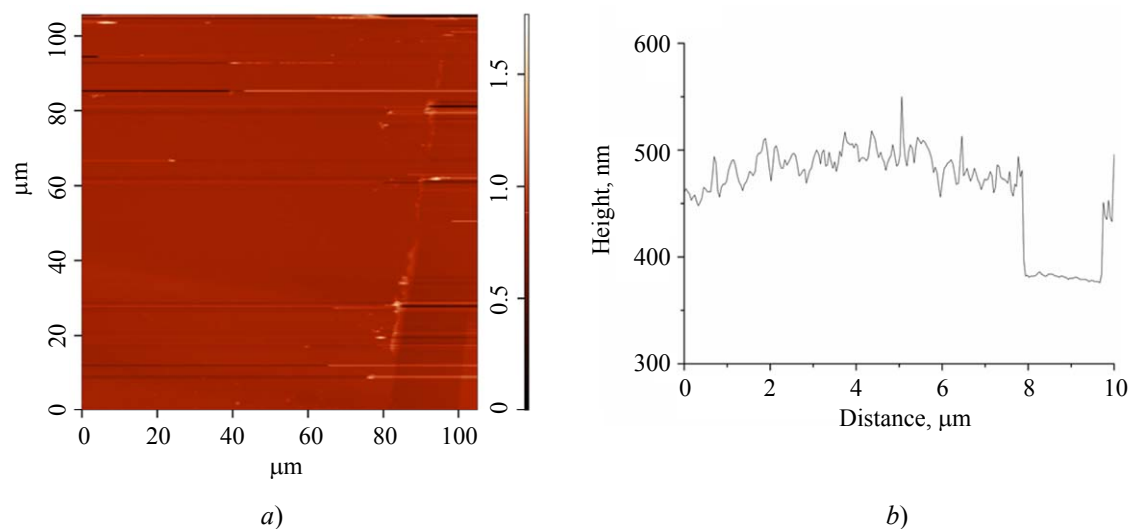


Fig. 5. Surface image and film cross-section profile obtained by depositing AgInS_2 CQD inks

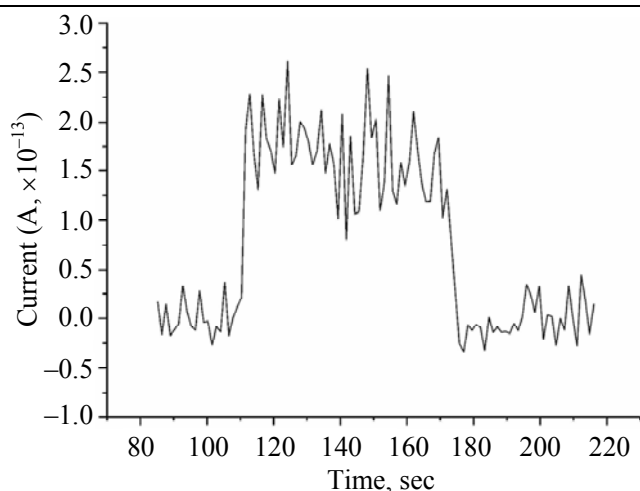


Fig. 6. Typical dependence of current on time when switching on and off illumination from a 405 nm source

Conclusions

For the first time, inks for direct printing of photosensitive structures were obtained based on colloidal AgInS₂ nanocrystals. For this purpose,

a new method for the in-solution exchange of long-chain ligands for short-chain ones was developed for AgInS₂ nanoparticles. It was demonstrated that AgInS₂ nanoparticles with this type of ligand shell are highly suitable for ligand exchange aimed at ink formulation. We established that the carboxylate ligand shell allows the required ligand exchange to be carried out efficiently and completely for produce inks. The obtained inks were deposited using a microplotter onto interdigitated electrodes, resulting in the fabrication of a photosensitive structure of the photoresistive type, which showed a clear photoresponse under exposure to monochromatic radiation with a wavelength of 405 nm.

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