Synthesis of ternary chalcogenide colloidal nanocrystals in aqueous medium

D S Mazing, I S Chernaguzov, A I Shulga, O A Korepanov, O A Aleksandrova, V A Moshnikov
Saint Petersburg Electrotechnical University "LETI", ul. Prof. Popova, 5, 197376 Russia
E-mail: dmazing@yandex.ru.

Abstract. Colloidal nanocrystals of AgInS$_2$, Zn-Ag-In-S were synthesized directly in an aqueous medium by injection method. Two ligands, L-Glutathione and sodium citrate, were used for preparation of precursor solutions to achieve a balance of the reactivity of the two types of cations. Obtained samples are characterized by asymmetric photoluminescence band, tunable depending on the conditions of the synthesis.

1. Introduction
Semiconductor quantum dots (QD) play important role in founding new functional materials with better optical and electrical properties. The majority of QDs for visible and near-infrared range is based on binary compounds. These QDs contain toxic heavy metals such as Cd, Pb or Hg. Using heavy metals can limit the application of QD technology in household appliances and especially in biomedicine. Nanocrystals of ternary chalcogenide compounds I-III-VI (CuInS$_2$, AgInS$_2$) and its quaternary modifications may be a substantially less toxic alternative.

They are characterized by a wide tuning range of absorption and emission bands, a large Stokes shift and long lifetime of the excited state. The most significant drawback of this type of nanocrystals is the large full-width at half maximum of the emission band (usually> 80 nm). Synthesis of ternary chalcogenide nanocrystals in a nonpolar organic medium has recently seen significant progress [1,2]. However, in view of biomedicine applications direct production of the nanoparticles in aqueous solutions is of great interest [3,4].

2. Materials and methods
Silver nitrate (AgNO$_3$), indium(III) nitrate hydrate (In(NO$_3$)$_3$$\cdot$4.5H$_2$O), L-Glutathione, sodium citrate, sodium sulfide hydrate (Na$_2$S$\cdot$9H$_2$O), zinc nitrate hydrate (Zn(NO$_3$)$_2$$\cdot$6H$_2$O) were used as purchased without additional purification.

Absorption spectra were acquired on a PE-5400UV UV–vis spectrophotometer (LLC “Ekohim”). Photoluminescence measurements were carried out on spectrofluorimeter based on monochromator MDR-206 (LOMO) using laser excitation $\lambda = 445$ nm.

3. Experiment and results
Adjusting the reactivity of various cationic precursors is critical to avoid phase separation in the synthesis of multicomponent CuInS$_2$ and AgInS$_2$ nanocrystals. Hydrophobic 1-dodecanethiol have been extensively used to balance the reactivity of copper or silver and indium precursors in organic media. However, the difference of reactivity between Ag$^+$(Cu$^+$) and In$^{3+}$ ions is expected to be even more significant in aqueous solution. According to the hard and soft acids and bases (HSAB) theory, Ag$^+$(Cu$^+$) is a soft acid, whereas In$^{3+}$ is hard. Water-soluble thiols, such as L-glutathione and 3-mercaptopropionic acid, are soft bases (due to the presence of a sulfhydryl group) and their complex with In$^{3+}$ hard acid have a low stability. As a result, phase separation may occur if water-soluble thiols are used as the sole complexing agent. To reduce the reactivity of the In$^{3+}$ ion, a hard ligand which
contains polycarboxylate groups, such as sodium citrate may be introduced [4]. Therefore, in this work both L-glutathione and sodium citrate are used as stabilizing agents for the synthesis of water-soluble colloidal nanocrystals of AgInS$_2$ and Zn-Ag-In-S.

The synthesis protocol was based on the method described in [4]. Colloidal nanocrystals of AgInS$_2$ were prepared with various ratios of cation precursors [Ag]:[In]. For [Ag]:[In] = 1:4 feeding ratio 0.005 mmol of AgNO$_3$ and 0.02 mmol of In(NO$_3$)$_3$·4.5H$_2$O were dissolved in 5 ml of H$_2$O and loaded into 10 ml flask. Thereafter 0.01 mmol of L-glutathione and 0.08 mmol of sodium citrate (200 μl of an aqueous solution) were added to this solution. The anionic precursor solution was obtained by dissolving 0.04 mmol of Na$_2$S·9H$_2$O in 500 ul distilled water. The sulfur precursor solution was injected into the stock solution at room temperature, then heated up to 95 ° C for 40 minutes. For ZnS shell deposition initial solution of the nanocrystal cores was cooled to room temperature and 0.02 mmol of Zn(NO$_3$)$_2$·6H$_2$O in 200 ul of distilled water was injected into the flask followed by dropwise addition of 0.02 mmol Na$_2$S·9H$_2$O. The mixture was heated up to 95°C for 40 minutes. The same synthesis protocol was used for other ratios of cation precursors.

Optical properties of colloidal nanocrystals of ternary compounds have strong composition dependence. Synthesis of AgInS$_2$ was done at various molar ratios of metal cations. These aqueous samples were investigated using absorption and photoluminescence spectroscopies. Figure 1 shows the PL spectra of samples with different feeding ratio of cation precursors.

![Photoluminescence spectra of colloidal nanocrystals of AgInS$_2$ prepared with different Ag$^+$ to In$^{3+}$ molar ratios.](image)

Emission band of synthesized nanocrystals consists of at least two subbands with low energy band tending to become more intensive relative to higher energy band with increasing Ag to In ratio. Surface states and internal traps have a huge impact on the observed broad and asymmetric PL spectrum. This issue was considered in detail in work [5] on AgInS$_2$ colloidal nanocrystals obtained in a nonpolar medium. The authors of this work investigated the changes in the emission spectra as a function of the growth time (size) of nanocrystals using time-resolved photoluminescence spectroscopy. They have shown that the two main emission bands making up the spectrum can be associated with radiative recombination through low-lying surface traps (the lifetime of the excited
state is ~ 50 ns) for relatively high-energy segment of the spectrum and deep defect levels for the lower energy region (the lifetime of the excited state is ~ 220 ns). The intensity of the bands was redistributed in favor of emission through deep centers during the growth of nanocrystals [5].

The ratio of cations in the reaction volume was varied in our experiment, and the observed change in the shape of the PL spectrum in terms of the conclusions made in [5] is counterintuitive, taking into account that a decrease in the mole fraction of Ag⁺ should lead to an increase in the concentration of silver vacancies and substitutional impurities of In₂Ag⁺ type which form deep acceptor levels. On the other hand there is possibility that concentration variation of cationic species affects not only resulting composition but also mean size of crystallites. As smaller QDs have higher surface area to volume ratio this may account for the dominance of shorter wavelength PL band at lower [Ag⁺]:[In] precursor content signifying higher input of surface defects in resulting PL. To clarify the mechanisms of PL and the evolution of spectra in our hydrophilic samples, it makes sense to make measurements by the method of time-resolved photoluminescence spectroscopy, which will allow us to estimate the lifetime for different sections of the PL band and to draw a conclusion about emission nature.

In this experiment, the Zn-In-S cores were first obtained, after which various amounts of silver dopant were introduced. For this 0.02 mmol of Zn(NO₃)₂·6H₂O and 0.02 mmol of In(NO₃)₃·4.5H₂O in 5 ml of H₂O and loading into 10 ml flask. Thereafter 0.04 mmol of L-glutathione and 0.08 mmol of sodium citrate (200 μl of an aqueous solution) were consequentially added to this solution. The anionic precursor solution was obtained by dissolving 0.04 mmol of Na₂S·9H₂O in 500 μl of distilled water. The sulfur precursor solution was injected into the stock solution at room temperature, then heated up to 95°C for 40 minutes. AgNO₃ precursor was dropwise added to the resulting solution of the cores so that the percentage mole ratio of Ag to In was 2.5%. The solution was heated up to 95 °C for 4 hours. The same synthesis protocol was used for 5% and 10% ratios of cation precursors. Figure 2 shows the absorption and PL spectra of samples obtained with different amount of silver precursor.

![Figure 2](image_url)

**Figure 2.** Absorption (on the left) and PL (on the right) spectra of Zn-Ag-In-S colloidal nanocrystals.

As can be seen from the photoluminescence spectra with increasing content of Ag⁺, the absorption edge and the emission maximum shift to the long-wavelength region. It is suggested that Ag⁺ has a higher rate of cation exchange with Zn²⁺ than with In³⁺ cations, which may result from bond of sulfur with indium being stronger than with zinc. The highest occupied molecular orbital (HOMO) of Zn-In-S consists of a hybrid of S 3p and In 5s5p orbitals, while the levels of the lowest unoccupied molecular orbital (LUMO) are formed from S 3p hybridized with Zn 3d. After the addition of Ag⁺ cations of Zn²⁺ are partially replaced and the HOMO levels rise due to the strong interaction of the wave function of Ag 4d and S 3p. As a result band gap is reduced [6].
4. Conclusion

Colloidal nanocrystals of AgInS$_2$ and Zn-Ag-In-S were directly synthesized in aqueous medium employing L-glutathione and sodium citrate as ligands. Photoluminescence of synthesized nanocrystals consists of two or more subbands and is of defect nature. It exhibits strong dependence on the ratio of cationic precursors so that with increasing silver content emission bands shift to longer wavelength region. Additional investigations by means of time resolved photoluminescence spectroscopy may help to elucidate exact mechanism of emission and its dependence on the cation ratio.

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