AgInS$_2$/ZnS nanocrystals as an active medium for cobalt detection

O A Korepanov, D S Mazing, O A Aleksandrova and VA Moshnikov
Micro- and nanoelectronics department Saint Petersburg Electrotechnical University "LETI" St. Petersburg, Russia

Abstract. In this work, the effect of photoluminescence (PL) quenching of ternary chalcogenide AgInS$_2$ nanocrystals (NCs), as well as the core/shell structure, with variation of the cobalt ions (Co$^{2+}$) concentration in aqueous solution, was studied. The quenching effect is described using the Stern-Volmer equation. The PL spectra were modelled in the range of 450–800 nm using four Gaussian functions, which makes it possible to identify several bands of the PL spectrum.

1. Introduction
Heavy metals pose a threat to the environment and human health. These include cadmium, lead, mercury, nickel, cobalt, etc. Both the metals themselves and their compounds may have carcinogenic and mutagenic effects. In environmental monitoring in agriculture, in industrial production, rapid or express analysis methods are lacking. It requires the development of inexpensive portable devices, the principal element of which is an active sensor for detection of heavy metal ions. Currently, for these purposes, much attention is paid to the development of luminescent methods of analysis, which have a sufficiently high sensitivity, are feasible and relatively inexpensive. Colloidal solutions of nanocrystals based on metal chalcogenides [1,2,3] appear promising as an active medium for detectors of heavy metal ions.

2. Experiments and results
In this work, AgInS$_2$/ZnS NCs are used, which were obtained in the aqueous medium with 3-Mercaptopropionic acid as a ligand, the synthesis technique is described in detail in [4,5]. The photoluminescence of these NCs is characterized by a broad emission spectrum in the visible region. The size distribution of the AgInS$_2$/ZnS nanocrystals obtained with particle size analyzer Photocor Mini is presented on the Figure 1. The size distribution has an asymmetric form with the maximum at 3 nm.

The Co$^{2+}$ ions detection was performed as follows: AgInS$_2$/ZnS particles in phosphate-buffered saline were placed into Eppendorf vials, after that solutions of Co$^{2+}$ cations in a volume of 50 μl were added. The amount of AgInS$_2$/ZnS particles was constant, the pH of the solution in the investigated concentration range was equal to 7.4. The source of Co$^{2+}$ ions was cobalt (II) nitrate, which was dissolved in water to obtain different concentrations. The PL spectra of AgInS$_2$/ZnS NCs with different concentrations of Co$^{2+}$ ions are given in Figure 2 (left). The same results normalized to the spectrum of the pure NCs solution are presented in Figure 2 (right).
Figure 1. The size distribution of the AgInS$_2$/ZnS nanocrystals, obtained by the method of dynamic light scattering.

Figure 2. (left) PL spectra of NCs AgInS$_2$/ZnS in the presence of different concentrations of Co$^{2+}$ ions; (right) The same spectra normalized to the emission of the pure solution.

In the presence of Co$^{2+}$ the quenching of the PL is accompanied by the intensity redistribution of the PL maxima, and the small redshift of emission maximum is observed. The spectrum shift is another possible parameter for selective detection of heavy metals in the solutions. In the previous work [5], repositioning of spectrum maxima to the UV-region was observed with the addition of nickel cations in the investigation range of up to 3.47 mmol/L.

Co(II) quenches the photoluminescence of AgInS$_2$ NCs in a concentration-dependent manner that is described by the Stern–Volmer equation (1), which is given by the following equation:

$$I/I_0 = 1+K_v[Q]$$

$I_0$ and $I$ are the PL integral intensities in the absence and presence of different concentrations $[Q]$ of Co$^{2+}$ ions in the solution of AgInS$_2$ NCs, $K_v$ is the Stern–Volmer quenching constant. The Stern–Volmer plot is exhibited in Figure 3. (left)

The decomposition of asymmetric PL spectra makes it possible to qualitatively evaluate various radiative recombination paths. Figure 3 (right) shows the decomposition results of the PL spectra of AgInS$_2$/ZnS NCs without cations in the solution, as well as in the presence of 1.36 mmol/L Co$^{2+}$ ions. Linear approximation allows the quantitative and qualitative analysis for the cations present in the solution. In this case, the approximating lines are straight, the angles of inclination of which are different.
The Stern–Volmer quenching constants are equal to 7.155 and 0.855, respectively for cobalt and nickel cations.

According to the results of the PL spectrum decomposition, it can be seen that the redistribution of the PL spectra occurs due to an increase of the right peak (green lines) (Figure 3 (right)), which is contrary to the results obtained earlier in a study of the effect of nickel cations on the same solution.

Addition of cobalt cations to the AgInS$_2$ cores solution was also performed using cobalt nitrate. The volumes of the studied samples and the pH of the system had not been changed. The PL spectra of AgInS$_2$ NCs with different concentrations of Co$^{2+}$ ions are shown in Figure 4 (left). The same results normalized to a pure solution of NCs are presented in Figure 4 (right).

![Figure 3](image1.png)

**Figure 3.** (left) The Stern–Volmer plot of AgInS$_2$/ZnS NCs PL spectra in the presence of different concentration of Ni$^{2+}$ and Co$^{2+}$ cations. The green triangles show the data for the presence of Co$^{2+}$ ions, red circles for Ni$^{2+}$ ions [5]. (right) PL spectra of AgInS$_2$/ZnS NCs (black curves) and modelling results by Gaussian decomposition (colour curves). The solid lines correspond to the pure solution, dash lines correspond to the solution in the presence of Co$^{2+}$ ions at concentration 1.36 mmol/L.

![Figure 4](image2.png)

**Figure 4.** (left) PL spectra of NCs AgInS$_2$ (core) in the presence of different concentrations of Co$^{2+}$ ions in the aqueous medium; (right) The same spectra normalized to the emission of the pure solution.
The quenching of the PL is similarly described by a straight approximating line according to the Stern-Volmer (1) equation (Figure 5).

Figure 5. The Stern–Volmer plot of PL spectra of AgInS$_2$ NCs (cores) in the presence of Co$^{2+}$ ions.

Figure 6 shows the decomposition results of the PL spectra AgInS$_2$ (cores) NCs without any cations (left), as well as in the presence of 0.85 mmol/L Co$^{2+}$ ions (right).

Figure 6. (left) PL spectra of the pure AgInS$_2$ (cores) NCs solution (black curves) and modelling results by Gaussian decomposition; (right). PL spectra of the AgInS$_2$ (core) NCs solution (black curves) in the presence of Co$^{2+}$ ions at concentration 0.85 mmol/L and modelling results by Gaussian decomposition.

As can be seen from the results of the decomposition of the PL spectra Figure 6. (right), a regular decrease occurs only for the intensity of the right PL maximum (green lines). The intensity is redistributed between the peaks, but unlike the core/shell structure, the intensity of the right peak decreases faster than the left one.

3. Conclusion
The effect of cobalt cations on the PL properties of AgInS$_2$ (cores) NCs, as well as particles, coated by ZnS shell, was investigated. The quenching of the PL spectra is described by the Stern–Volmer equation and approximated as straight lines. The difference in the Stern–Volmer quenching constants allows
selectivity between the cobalt and nickel cations. The redistribution of the PL maxima of the spectra is different for core-shell and uncovered nanoparticles: for the AgInS$_2$/ZnS, the right peak increases, and for AgInS$_2$ (cores) there is a decrease. The results can be useful for development of optical sensors for heavy metal ions.

Acknowledgments
Authors thank Dr Alexei Soloviev for performing dynamic light scattering measurements.

References
[1] Vázquez-González M and Carrillo-Carrion C 2014 *J. Biomedical Optics* **19**(10) 101503
[2] Podgurska I, Rachkov A and Borkovska L 2018 *physica status solidi (a)* **215**(3) 1700450
[3] Zi Y, Huang Y, Yan Z and Liao S 2014 *Journal of Luminescence* **148** 359-63
[4] Mazing D S, Korepanov O A, Aleksandrova O A and Moshnikov V A 2018 *Optics and Spectroscopy* **125**(5) 773-76
[5] Korepanov O A, Mazing D S, Aleksandrova O A and Moshnikov V A 2019 *IEEE Conference of Russian Young Researchers in Electrical and Electronic Engineering (EIConRus)* p 771