The effect of lead and nickel cations on AgInS$_2$/ZnS nanocrystals photoluminescence in aqueous solution

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Abstract. A sensing fluorescent probe based on the photoluminescence (PL) quenching of the AgInS$_2$ colloidal nanocrystals (NCs) with a wide bandgap ZnS shell was studied for lead ions detection. The results were compared with the work where the influence of nickel ions presence on PL was studied. Addition of lead cations was accompanied by decreasing of PL intensity of the AgInS$_2$/ZnS NCs and redshift of maxima of PL spectra. The quenching effect was described by the Stern–Volmer relationship. The obtained results could be useful for the development of new express-methods for heavy metal detection in aqueous media.

1. Introduction

Environmental pollution with heavy metals is one of the leading problems of ecology. All heavy and transition metals are pollutants, the observation of which is mandatory in all environments since at high concentrations these elements have a negative impact on human health.

Traditional methods of the heavy metal ions concentration detection require a lot of time, expensive equipment and qualified personnel. In recent years, express-methods for analyzing the presence of heavy metal ions in environmental and biological samples have been actively developed. One of the promising directions is the development of fluorescent sensors based on the quenching effect of luminescence in the presence of heavy metal ions [1].

In this work, the quenching effect of PL of water-soluble AgInS$_2$/ZnS nanocrystals (NCs) and the shift of the PL spectra in the presence of Pb$^{2+}$ and Ni$^{2+}$ ions were studied. The main advantages of using AgInS$_2$/ZnS NCs are a wide range of emission spectra and photochemical stability. Their water solubility makes them potentially compatible with biological applications. This paper explores the possibility of using AgInS$_2$/ZnS NCs as active media for heavy metal ions sensing.

2. Experiments and results

AgInS$_2$/ZnS NCs were synthesized in aqueous solution [2,3]. AgNO$_3$ (0.2 mmol) and 3-mercaptopropionic acid (4 mmol) were dissolved in 5 ml of distilled water. The solution of 25% NH$_4$OH (0.45 ml) was added followed by an aqueous solution of InCl$_3$ (0.8 mmol). At room temperature 1 mmol of Na$_2$S-9H$_2$O were injected rapidly resulting in instantaneous nucleation. The mixture was heated up to 100°C for 30 minutes.

To coat thus obtained nanoparticles with ZnS shell complexes of Zn$^{2+}$ with 3-mercaptopropionic acid (1 mmol) were added to the nanoparticle solution followed by dropwise addition of Na$_2$S-9H$_2$O (1 mmol). A certain amount of NaOH was used to raise pH and make the mixture translucent. The solution was then heated up to 100°C for 30 minutes. Nanoparticles were precipitated by addition of 2-
propanol followed by centrifugation and redispersed in distilled water or phosphate-buffered saline for further experiments and studies.

An analogous approach was used for the preparation of AgInS$_2$ nanoparticles using L-Glutathione as a surfactant with various ratios of cation precursors [Ag]:[In]. For the ratio [Ag]:[In] = 1:4 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. 0.01 mmol of L-Glutathione and 0.08 mmol of sodium citrate were added to the solution. Nucleation was performed by injecting of 0.04 mmol of Na$_2$S·9H$_2$O. The solution was heated up to 95 °C for 40 minutes. The same protocol was used for synthesis with [Ag]:[In] = 1:20 and [Ag]:[In] = 1:1.

Figure 1. Normalized PL spectra of AgInS$_2$/ZnS NCs

PL measurements were carried out on spectrofluorometer based on MDR-206 monochromator using laser excitation on $\lambda = 405$ nm. As can be seen from fig. 1, the PL spectra AgInS$_2$/ZnS NCs are characterized by a wide PL spectrum (100–150 nm) in the wavelength range of 500–800 nm and have two characteristic maxima.

Figure 2. PL spectra of AgInS$_2$ NCs synthesized with L-Glutathione as a ligand.
By changing the ratio of the constituent components of the AgInS$_2$ NCs, in particular [Ag] and [In], it is possible to achieve the most desirable shape of the spectrum (the position of the PL maxima and their intensity) [4]. With increasing Ag concentration in the solution, the position of the low-energy luminescence peak shifts to the long-wavelength region, which indicates that NCs with a high Ag content have narrower band-gap, which is attractive from the point of view of the application in biomedical research. The nature of multiple PL bands is not clear. The short-wave peak is presumably associated with the surface-related states of NCs and the long-wave peak – with internal defects [5].

In sensors, complex forms of the spectrum are preferable, since they allow a qualitative analysis of the metal cations present in the NCs solution with greater accuracy due to the redistribution of the intensities of the maxima of the PL spectra.

In these experiments to assess the effect of heavy metal ions on the PL quenching of AgInS$_2$/ZnS NCs in aqueous solution, AgInS$_2$/ZnS NCs with a molar ratio of [Ag]:[In] = 1:4 stabilized by 3-mercaptopropionic acid were used.

The source of the Pb$^{2+}$ ions was lead (II) chloride, which was dissolved in distilled water to obtain different concentrations. The experiments were performed in the medium of phosphate-buffered saline, containing a constant amount of AgInS$_2$/ZnS NCs. The final volume in each case was 1 ml; the pH of the medium in the investigated concentration range was equal to 7.4. The addition of Pb$^{2+}$ ions to the solution resulted in a decrease of the PL intensity. Nickel ions were introduced in a similar way, where nickel (II) chloride was used as an ion source. Addition of nickel cations from nickel chloride in the solution results in changing of transparency and colour of the medium. The solution became yellowish and turbid [6]. As a result due to the low solubility of lead chloride in water, the experiment was performed in a narrow range of concentrations.

The quenching effect of Pb$^{2+}$ and Ni$^{2+}$ is described using the Stern-Volmer equation (1):

\[
\frac{I}{I_0} = 1 + \frac{K_{sv}}{C_{Me^{2+}}}
\]

$I_0$ и $I$ are PL intensities for the pure solution of AgInS$_2$/ZnS NCs and in the presence of different concentrations $C_{Me^{2+}}$ of divalent metal cations, $K_{sv}$ is the Stern–Volmer quenching constant.

Figure 3 (left) shows the Stern-Volmer relationship (1) for AgInS$_2$/ZnS in the presence of nickel and lead cations. The approximating functions coincide at low concentrations of lead ions obtained using lead chloride. The Stern-Volmer constant is 7.87. The same results were obtained using lead cations from lead chloride with a concentration up to 0.48 mmol/L. Due to the low solubility of lead chloride in water at room temperature, it was not possible to investigate the effect of lead cations on the PL of AgInS$_2$/ZnS NCs in a wide concentration range. Therefore, it wouldn’t be possible to distinguish these metals in the solution. In addition to quenching of the PL, a blueshift of the PL spectrum is observed for nickel. This shift was 32 nm in the range of nickel ions concentration from 0 to 3.74 mmol/L. Using lead (II) nitrate as a source of lead cations, the PL spectrum was obtained at a concentration of 3.62 mmol/L. In this case, the shift was towards longer wavelength accompanied by the opposite PL spectrum rearrangement. Figure 3 (right) shows the PL spectrum of a solution without heavy metal ions, a solution containing lead cations with concentration 3.41 mmol/L, and a solution containing 3.62 mmol/L of nickel cations [6].
Figure 3. (a) The Stern–Volmer relationship for aqueous solutions of AgInS$_2$/ZnS NCs with Ni$^{2+}$ and Pb$^{2+}$ ions; (b) Normalized PL spectra of AgInS$_2$/ZnS NCs in presence of Ni$^{2+}$ and Pb$^{2+}$.

The decomposition of complex shapes of the spectra could be done using at least four Gaussians.

Figure 4. The decomposition results of normalized PL spectra of AgInS$_2$/ZnS NCs.

Black solid lines correspond to the pure solution; blue dash lines correspond to the solution in the presence of Ni$^{2+}$ cations; red dash lines - to the solution in the presence of Pb$^{2+}$ cations.

From fig. 4, it can be seen that the most significant shift in the PL spectra occurs for a short-wave maximum. This can be related to the interaction of heavy metal cations with free surface states, having an impact on the process of luminescence quenching.
3. Conclusion

As a result, with the addition of various metal ions to the AgInS$_2$/ZnS NCs solution, the quenching of the PL is observed. Furthermore, there is a change in the shape of the spectrum and its position. The addition of nickel cations leads to a blueshift of the PL spectrum with the decreasing of the low energy peak of the PL band. The addition of lead nitrate causes the opposite effect: there is a PL redshift with a relative increase of the low energy peak intensity. It can be assumed that the addition of nickel ions primarily changes the maximum associated with surface states, which results in a shift of high energy maximum towards shorter wavelengths. The addition of lead ions leads the opposite results, primarily due to the formation of deep-level centres in NCs or the occurrence of additional paths for nonradiative recombination.

These effects suggest possible selectivity of the method for heavy metal ions detection in aqueous solutions. However, further studies are needed to study the physicochemical processes of the interaction of heavy metal ions with AgInS$_2$/ZnS NCs.

References

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