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PACS 78.55.-m ,81.07.Ta
DOI http://dx.doi.org/10.18524/1815-7459.2017.1.96438

INFLUENCE OF HEAVY METAL IONS ON THE PHOTOLUMINESCENCE OF NANOCRYSTALS $AgInS_2/ZnS$

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Abstract. The influence of ions of heavy metals Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, and ions, which are common components of natural and drinking water (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) on the photoluminescence of nanocrystals $AgInS_2$ with ZnS shell (NCs $AgInS_2/ZnS$) was investigated. Experimental data obtained confirm the assumption on the relationship between the level of quenching of NCs $AgInS_2/ZnS$ photoluminescence under exposure to the heavy metal ions and solubility constant of their sulfides. The concentration of ions Cu^{2+}, which caused a statistically significant quenching of NCs $AgInS_2/ZnS$ photoluminescence, is below their maximum allowable concentration in natural waters. It opens up prospects of NCs $AgInS_2/ZnS$ for developing methods for environmental monitoring of the copper ions.

Keywords: nanocrystals, photoluminescence, quenching, ions of heavy metals

ВПЛИВ ІОНІВ ВАЖКИХ МЕТАЛІВ НА ФОТОЛЮМІНЕСЦЕНЦІЮ НАНОКРИСТАЛІВ $AgInS_2/ZnS$

І. Подгурська, А. Рачков

Анотація. Було досліджено вплив іонів важких металів Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, та іонів, які є звичайними компонентами природної і питної води (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) на фотолюмінесценцію нанокристалів $AgInS_2$ з оболонкою ZnS (НК $AgInS_2/ZnS$). Отримані експериментальні дані підтверджують припущення про взаємозв'язок між рівнем гасіння фотолюмінесценції НК $AgInS_2/ZnS$ під впливом іонів важких металів та величиною константи розчинності їх сульфідів. Концентрація іонів Cu^{2+}, що викликає статистично значуще гасіння фотолюмінесценції НК $AgInS_2/ZnS$, виявилась нижчою за їх гранично допустиму концентрацію в природних водах. Це відкриває перспективи НК $AgInS_2/ZnS$ для розробки методів екологічного моніторингу іонів міді.

Ключові слова: нанокристали, фотолюмінесценція, гасіння, іони важких металів

ВЛИЯНИЕ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ НА ФОТОЛЮМИНЕСЦЕНЦИЮ НАНОКРИСТАЛЛОВ $AgInS_2/ZnS$

И. Подгурская, A. Rachkov

Аннотация. Было исследовано влияние ионов тяжелых металлов Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, и ионов, которые являются обычными компонентами природной и питьевой воды (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) на фотолюминесценцию нанокристаллов $AgInS_2$ с оболочкой ZnS (НК $AgInS_2/ZnS$). Полученные экспериментальные данные подтверждают предположение о взаимосвязи между уровнем гашения фотолюминесценции НК $AgInS_2/ZnS$ под воздействием ионов тяжелых металлов и величиной константы растворимости их сульфидов. Было выявлено, что концентрация ионов Cu^{2+}, вызывающая статистически значимое гашение фотолюминесценции НК $AgInS_2/ZnS$, оказалась ниже их предельно допустимой концентрации в природных водах. Это открывает перспективы НК $AgInS_2/ZnS$ для разработки методов экологического мониторинга ионов меди.

Ключевые слова: нанокристаллы, фотолюминесценция, гашение, ионы тяжелых металлов

Introduction

The development of industry, transport and intensive use of various chemicals in agriculture made an environmental monitoring as a very actual and necessary task. Ions of heavy metals are among the most dangerous and common environmental pollutants. They are characterized by high stability, solubility in precipitation, and absorption capacity for soil and plants [1-4]. Their accumulation in humans and animals can cause the development of various pathologies: cancer, blood disorders, diseases of endocrine system and so on.

Conventional methods of analysis of heavy metals, such as various types of chromatography and spectrometry, require highly qualified personnel, sophisticated and expensive equipment. Therefore, the development of simple to use, accurate, fast and cheap method for determining the concentration of heavy metals in samples of natural water or food is urgent and important task. To develop such methods, quantum dots, which are semiconductor nanocrystals (NC) capable of photoluminescence may be used [2].

They usually consist of 10^3 - 10^5 atoms and have a size of 1 to 12 nm. Photoluminescent NC often built with a core represented a relatively narrow-band semiconductor material and a shell with a wide-gap semiconductor such as ZnS or ZnSe, which provides greater photostability and higher quantum yield. The core of nanocrystals may consist of atoms of elements II - VI (ZnS, CdS, CdSe, HgS), III - V (GaAs, InP, InAs, GaN), IV - VI (PbTe, PbSe) groups. Also a core can be formed by ternary compositions CdZnS, CdSSe, InNP, InGaAs, etc. [2-6].

Recently, the researchers from L.V. Pisarzhevsky Institute of Physical Chemistry of NAS of Ukraine developed the method for preparation of ternary NC $AgInS_2$, which is one of the best alternatives to NC based on Cd or Pb. Their advantages are low toxicity, a large band gap (from 1.87 to 2.03 eV) and high molar extinction coefficient. NC $AgInS_2$ used primarily for making photovoltaic devices, but recent studies have shown the prospect of using these quantum dots in cell imaging and analysis of certain substances[7].

The aim of this work is to investigate the influence of ions of heavy metals Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, and ions, which are common components of natural and drinking water (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) on the photoluminescence of nanocrystals $AgInS_2$, to figure out the possibility of the further use of the nanocrystals to determine the ion concentrations.

Materials and methods

To investigate the influence of metal ions on NC photoluminescence, aqueous solutions of $CuCl_2{\cdot}2H_2O$, $CoCl_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$, $AgNO_3$, NaCl, KCl, $CaCl_2$ and $MgCl_2{\cdot}6H_2O$ were used. All of the reagents were obtained from SC "Macrohim" Ukraine. To prepare the solution, the deionized water Milli-Q (type I, R = 18.2 MΩ cm) obtained by "Simplicity Water Purification" ("Millipore", USA) was used.

Nanocrystals $AgInS_2$ with ZnS shell (NCs $AgInS_2$/ZnS) were synthesized and kindly provided by the senior researcher of L.V. Pisarzhevsky Institute of Physical Chemistry of NAS of Ukraine, Dr. A. Raevskaya.

All photoluminescence measurements, except for obtaining spectra, were performed using scanning spectrofluorometer "Synergy HT Multi-Mode Microplate Reader" ("BioTek", USA). In experiments using immunological plates with a special non-binding surface that prevents sorption in its wells ("Greiner Bio-One", Germany). Aqueous solutions of NCs $AgInS_2$/ZnS (final dilution was 1:100) and the metal ions mixed in the desired concentrations in the wells of immunological plate. For photoluminescence excitation and emission measurement filters 460±40 nm and 590±20 nm, respectively, were used.

Photoluminescence spectra were obtained by spectrofluorometer «Cary Eclipse» («Varian», Australia) at the excitation wavelength 260 nm. Aqueous solutions NC $AgInS_2$/ZnS and cadmium ions of corresponding concentration were mixed in a quartz cell with optical path length of 1 cm. NC emission was recorded in the range 500 to 750 nm.

Results and Discussion

At the beginning of the investigations of the influence of the heavy metals ions on the photoluminescence of NC $AgInS_2$/ZnS, a qualitative visual experiment was conducted - solutions of

$CuCl_2$, $CoCl_2$, $Ni(NO_3)_2$, $ZnCl_2$ або $Cd(NO_3)_2$ were added into test tubes with the nanocrystals to a final concentration of 1mM (an appropriate amount of water was added into the control tube) and the tubes put under the rays of ultraviolet lamp. Obviously, the ions Cu^{2+}, Co^{2+} and Ni^{2+} caused the almost complete quenching of photoluminescence of NC $AgInS_2$/ZnS, ions Zn^{2+} did practically no effect on its level, and ions Cd^{2+} influenced on (to some extent) not only the intensity of photoluminescence, but also its color (Fig. 1).

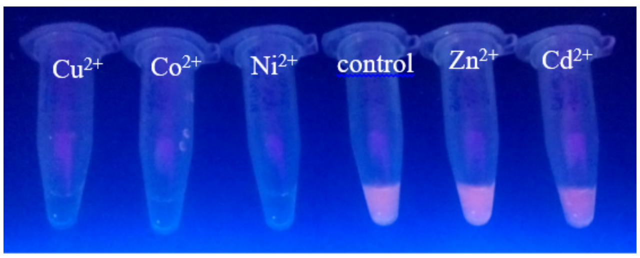

Fig. 1. Photoluminescence of NCs $AgInS_2$/ZnS in the presence of the ions Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}. Any ions were not added into the control test tube.

A more detailed quantitative experiment to study the effect of ions of nine different metals on photoluminescence of NC $AgInS_2$/ZnS was performed using scanning spectrofluorometer "Synergy HT Multi-Mode Microplate Reader" (Fig. 2).

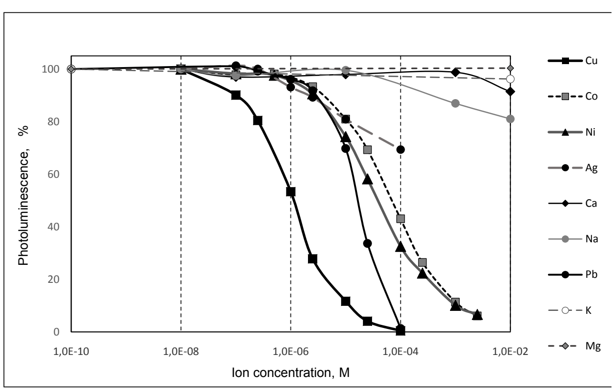

Fig. 2. Changes of normalized photoluminescence of NC $AgInS_2$/ZnS in the presence of ions Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Ag^+, Na^+, K^+, Mg^{2+} and Ca^{2+}. The values of measurement error is less than the size of the marks that have been used for plotting.

The results on the influence of ions that are normally found in natural bodies of water (Na^+, K^+, Mg^{2+}, Ca^{2+}), said that in relatively high concentrations (10 mM) only ions of sodium and calcium may cause some quenching photoluminescence (19% and 9% with confidence 99% and 95%, respectively). However, in natural fresh water concentration is typically less than 1 mM, and therefore should not significantly affect the level of photoluminescence NC $AgInS_2$/ZnS.

The strongest photoluminescence quenching happened in the presence of ions Cu^{2+}. Noticeable effect (statistically significant decrease in the intensity of photoluminescence of NC $AgInS_2$/ZnS) was observed when adding 0.25 μM Cu^{2+}, which is much lower than the permissible content of Cu^{2+} in natural waters. Ions Co^{2+}, Ni^{2+}, Pb^{2+}, Ag^+in the range of 0.5-10 μM caused nearly identical photoluminescence quenching.

Photoluminescence quenching of NC by heavy metal ions can be explained by the binding of ions on the surface of the nanocrystals, or rather, the inclusion of the metal ions to the crystal structure of zinc sulfide shell on the surface $AgInS_2$. The ions of other metals can displace zinc ions and integrate into the structure of the shell or join unpaired sulfur atoms on the surface of NC [9]. Substitution of zinc in zinc sulfide may depend on the solubility constant (K_{sp}) of heavy metal ion compounds with sulfur (II). If the solubility of the newly formed complex of metal with sulfur (II) is lower than the solubility of zinc sulfide, then this metal is able to fit into a shell of NC displacing of zinc ions and alter the intensity of photoluminescence due to decrease of luminescence centers on its surface.

As shown in the Table. 1, where negative logarithms of solubility constants of certain sulfides are, these figures are quite consistent with our experimental data on the influence of ions Cu^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} on photoluminescence of NC $AgInS_2$/ZnS. Silver ions did not quench photoluminescence stronger than other ions (which would be expected based on the lowest value K_{sp}) perhaps because they are components of core nanocrystals and their integration into crystal shell does not cause fundamental changes in its structure.

Table. 1.
Negative logarithms of solubility constants of the next sulfides [8].

Sulfides	-log K_{sp}
ZnS(β)	**21,6**
CoS(β)	24,7
NiS(γ)	25,7
PbS	26,6
CdS	27,8
CuS	35,2
Ag_2S	49,7

As for the role of ions Cd^{2+}, then an additional experiment was conducted: instead of the changes in photoluminescence of NC $AgInS_2$/ZnS at a fixed wavelength, the emission spectra in wide range of wavelengths were recorded (Fig. 3). Primary photoluminescence spectra of NC $AgInS_2$/ZnS (3-4 parallel measurements) for each Cd^{2+} concentration were averaged and fit (Fig. 3). It allows most accurately determine the maximum intensity of the photoluminescence spectrum and the corresponding wavelength.

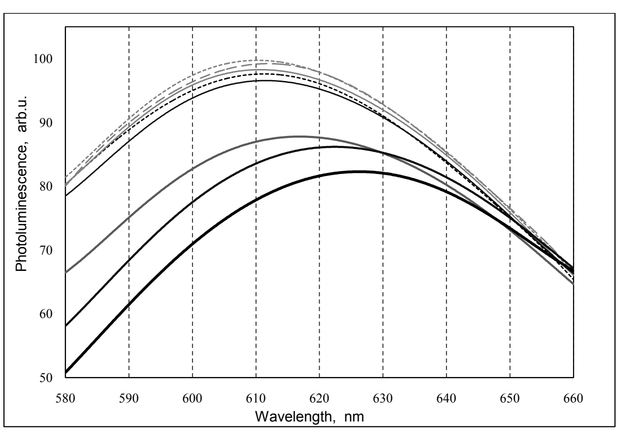

Fig. 3. Photoluminescence spectra of NC $AgInS_2$/ZnS in the presence of Cd^{2+} ions, from top to bottom 0 nM, 1 nM, 10 nM, 100 nM, 1 µM, 10 µM, 100 µM, 200 µM Cd^{2+}.

Thus, it was found that the addition of solutions containing Cd^{2+} to NC $AgInS_2$/ZnS caused some photoluminescence quenching (200 µM Cd^{2+} reduced the intensity of photoluminescence approximately on 18%) and shift of the photoluminescence peak about 16 nm (at no Cd^{2+} photoluminescence maximum was at 610 nm, after bringing Cd^{2+}concentration to 200 µM maximum shifted to 626 nm). The shift of the photoluminescence peak with a slight decrease in its intensity can be explained by the formation of new centers of photoluminescence on the surface as a result of substitution of zinc by cadmium in ZnS shell. This assumption is confirmed by the fact that the cadmium sulfide has a lower solubility constant compared with zinc sulfide, and should be largely replace the zinc ions in the shell of nanocrystals.

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Стаття надійшла до редакції 02.03.2017 р.

PACS 78.55.-m ,81.07.Ta
DOI http://dx.doi.org/10.18524/1815-7459.2017.1.96438

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Summary

The aim of this work is to investigate the influence of ions of heavy metals Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, and ions, which are common components of natural and drinking water (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}), on the photoluminescence of nanocrystals $AgInS_2$ with ZnS shell (NCs $AgInS_2/ZnS$) to figure out the possibility of the further use of the nanocrystals to determine the concentrations of the ions.

Photoluminescence measurements of NCs $AgInS_2/ZnS$ were performed using scanning spectrofluorometer "Synergy HT Multi-Mode Microplate Reader". Photoluminescence spectra were obtained by spectrofluorometer "Cary Eclipse".

Experimental data obtained confirm the assumption on the relationship between the level of quenching of NCs $AgInS_2/ZnS$ photoluminescence under exposure to the heavy metal ions and solubility constant of their sulfides. The order of studied ions by the degree of influence on the NC photoluminescence generally coincides with their order of the decrease of the solubility of their sulfides, with the exception of ions Cd^{2+} and Ag^{+}, which, when substituting zinc ions in the shell of nanocrystals may contribute to the formation of a certain amount of new centers of emission. The concentration of ions Cu^{2+}, which caused a statistically significant quenching of NCs $AgInS_2/ZnS$ photoluminescence, is below their maximum allowable concentration in natural waters. It opens up prospects of NCs $AgInS_2/ZnS$ for developing methods for environmental monitoring of the copper ions. Such methods have several advantages over conventional methods, among them - high sensitivity to nanomolar concentrations of copper ions, high speed of analysis and safety for both personnel and the environment.

Keywords: nanocrystals, photoluminescence, quenching, ions of heavy metals

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Реферат

Метою даної роботи є дослідити вплив іонів таких важких металів, як Cu^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ag^{+}, а також іонів, які є звичайними компонентами природної та питної води (Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}) на фотолюмінесценцію нанокристалів $AgInS_2$ з оболонкою ZnS (НК $AgInS_2/ZnS$), щоб з’ясувати можливість використання цих нанокристалів для визначення концентрацій зазначених іонів.

Вимірювання фотолюмінесценції НК $AgInS_2/ZnS$ були виконані з використанням сканувального спектрофлуориметра «Synergy HT Multi-Mode Microplate Reader». Спектри фотолюмінесценції були отримані за допомогою спектрофлуориметра «Cary Eclipse”.

Отримані експериментальні дані підтверджують припущення про взаємозв’язок між рівнем гасіння фотолюмінесценції НК $AgInS_2/ZnS$ під впливом іонів важких металів та величиною константи розчинності їх сульфідів. Порядок досліджуваних іонів за ступенем впливу на фотолюмінесценцію НК, як правило, збігається з порядком зменшення розчинності їх сульфідів, за винятком іонів Cd^{2+} і Ag^{+}, які, коли заміщують іони цинку в оболонці нанокристалів, можуть сприяти утворенню певної кількості нових центрів емісії. Концентрація іонів Cu^{2+}, що викликає статистично значуще гасіння фотолюмінесценції НК $AgInS_2/ZnS$, виявилась нижчою за їх гранично допустиму концентрацію в природних водах. Це відкриває перспективи НК $AgInS_2/ZnS$ для розробки методів екологічного моніторингу іонів міді. Такі методи мають ряд переваг в порівнянні з традиційними методами, серед них - висока чутливість до наномолярних концентрацій іонів міді, висока швидкість аналізу та безпека як для персоналу, так і для довкілля.

Ключові слова: нанокристали, фотолюмінесценція, гасіння, іони важких металів