PHYSICS AND CHEMISTRY OF SOLID STATE
V. 26, No.4 (2025) pp. 713-717
Section: Chemistry

DOI: 10.15330/pcss.26.4.713-717

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ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 26, № 4 (2025) С.713-717
Хімічні науки

UDC: 546.48'56-182:546.562:535

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

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Influence of Cu^{2+} ions on the optical properties of CdS/L-Cys colloid solutions

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The work investigated the effect of Copper (II) ions on the optical properties of colloidal solutions of Cadmium sulfide nanoparticles stabilized with L-Cysteine in aqueous solution at room temperature 25ºC. The introduction of Cu^{2+} ions into the reaction medium was carried out by ion exchange and co-precipitation methods.

It was found that the addition of solutions of Copper (II) salts of different concentrations to colloidal solutions of CdS nanoparticles causes agglomeration and, accordingly, a shift of the optical absorption edge to the long-wavelength region, an increase in the width of the forbidden bandgap of Cadmium Sulfide, and a decrease in the intensity of photoluminescence, except for a solution with a concentration of Copper (II) ions of $1 \cdot 10^{-5}$ mol/l.

Keywords: nanoparticles, colloidal solutions, heterostructures, optical properties, photoluminescence.

Received 04 June 2025; Accepted 27 October 2025.

Introduction

The creation of core-shell heteronanostructures based on the semiconductor CdS expands the possibilities of using such nanocrystals in various fields, including opto- and nanoelectronics, medical diagnostics, solar cells, photocatalysts, photosensors, and light-emitting devices. Many studies have been conducted on the possibility of doping CdS nanoparticles (NPs) with d-element cations Ag^{+}, Cu^{2+}, Zn^{2+}, Ni^{2+} [1-16]. The introduction of impurity ions into the reaction mixture is performed at different stages of the synthesis of semiconductor NPs and under different experimental conditions. As a result of the analysis of the literature on the preparation of CdS NPs doped with copper cations [3, 5, 9, 12, 14-16], there is no unambiguous result regarding the influence of Copper cations on the optical properties of Cadmium Sulfide nanoparticles. The change in the optical parameters of the studied system is influenced by the conditions of the experiment (synthesis temperature, pH value, order of introduction of precursors, ratio and concentration of crystal-forming ions and stabilizers). That is why the aim of this work is to investigate the effect of copper (II) ions on the optical properties of colloidal solutions of CdS/L-Cys NPs synthesized at room temperature.

I. Experimental

The synthesis of heterostructures was carried out on the basis of a previously synthesized and tested for stability colloidal solution with CdS nanoparticle with the addition of Copper (II) salts of different concentrations at different stages of synthesis (series of experiments 1 and 2).

Series of experiments 1 was carried out by ion exchange, i.e. by introducing Cu^{2+} cations into a solution of CdS/L-Cys NPs:

$$CdS/L-Cys + xCu^{2+} \rightarrow \left(Cd_{(1-x)}Cu_xS\right)/(L-Cys) + xCd^{2+} \quad (1)$$

Series of experiments 2 was carried out by the type of coprecipitation, by adding sulfide ions to a mixture of solutions

with Cadmium and Copper (II) cations:

$$(xCu^{2+} + yCd^{2+})/L - Cys + (x+y)S^{2-} \rightarrow (CdS)_y(CuS)_x/(L-Cys) \quad (2)$$

Synthesis according to both schemes was carried out using high-quality starting reagents, namely: 0.5 M solution of $CdCl_2 \cdot 2.5H_2O$ of the "high grade" grade, 0.05 M solution of "high grade" L-Cysteine; 0.5 M solution of $Na_2S \cdot 9H_2O$ (99% purity Aldrich), 0.1 M solution of NaOH, $1 \cdot 10^{-3}$ M solution of $Cu(NO_3)_2$ "CP".

In the experiments, colloidal solutions of CdS/L-Cys NPs with a fixed ratio of all precursors were used, namely $[Cd^{2+}]:[L\text{-}Cys]:[S^{2-}] = 1.1 : 2.2 : 1$. After draining the initial solutions of $CdCl_2$ reagents and L-cysteine, the pH of the solution was adjusted to 7. The ratio between the content of Cd^{2+}/Cu^{2+} ions was 400:1, 80:1 and 40:1.

All syntheses were carried out at a temperature of 298 K using deionized distilled water and without prior deaeration of the solutions.

The study of the optical properties of the solutions was carried out at a temperature of 298 ± 5 K using MDR-4 and USB-650 spectrophotometers (Ocean Optics). The optical density of the solutions was measured in the range of 0.01–2 with increasing wavelength in the range of 350–1000 nm. Photoluminescence (PL) was measured on a Perkin-Elmer LS55 luminescence spectrometer. All investigated solutions were excited by light with a wavelength of λ = 360 nm.

II. Results and Discussion

2.1. Study of the optical properties of the CdS/L-Cys/Cu^{2+} colloidal solution obtained by the ion exchange method

The results of the effect of adding Cu^{2+} ions (by ion exchange method, equation 1) to the reaction medium on the optical properties of CdS/L-Cys solutions are shown in Table 1 and Figure 1.

The introduction of copper ions into a colloidal solution of Cadmium Sulfide (series of experiments 1) causes a bathochromic shift of the optical absorption edge (Fig. 1, a), which generally causes a decrease in the Stokes shift.

A gradual increase in the concentration of Cu^{2+} ions in the reaction medium, above $5 \cdot 10^{-5}$ mol/l, has a more noticeable effect on the optical characteristics of the obtained systems.

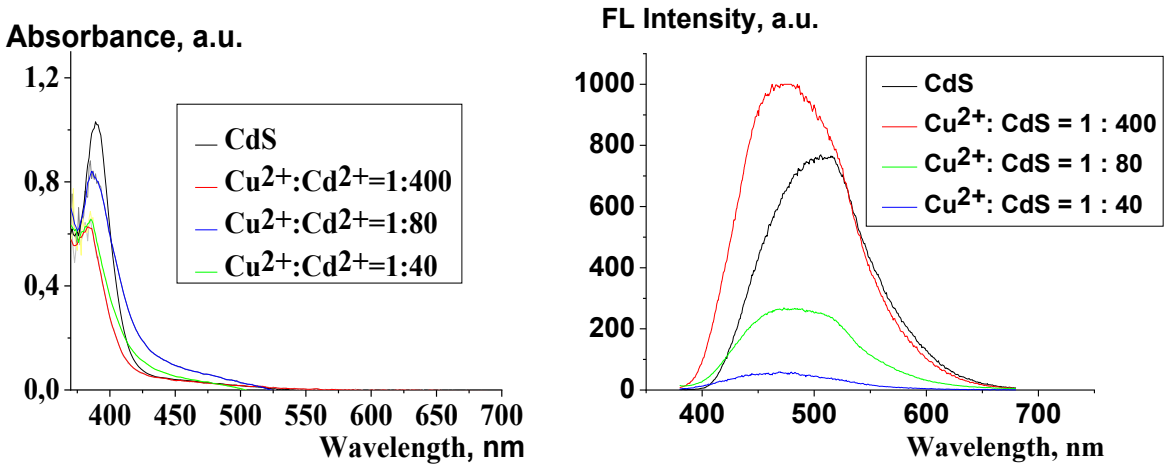
In particular, in the presence of Cu^{2+} ions, photoluminescence quenching occurs more noticeably, with the exception of the minimum concentration of $1 \cdot 10^{-5}$ mol/dm^3, which intensifies the photoluminescence of the obtained solution (Fig. 1, b).

Table 1.

Dependence of optical characteristics of CdS/L-Cys/Cu^{2+} systems on $[Cu^{2+}]$ (series 1)

№	$[Cu^{2+}]$, mol/l	$[Cd^{2+}]/[Cu^{2+}]$	λ_{lim} nm	λ_{max} nm	$\lambda_{max.lum}$ nm	Stokesland slide, nm	E_g, eV
1	0	-	409	389	506	117	3,04
2	$1 \cdot 10^{-5}$	400	410	384	474	90	3,03
3	$5 \cdot 10^{-5}$	80	416	387	484	97	2,99
4	$1 \cdot 10^{-4}$	40	418	385	469	84	2,97

Note: λ_{lim} - optical absorption edge, λ_{max} - optical absorption maximum, $\lambda_{max.lum}$ - luminescence maximum, Eg – bandgap.



a b

Fig. 1. Optical absorption (a) and luminescence (b) spectra of the CdS/L-Cys/Cu^{2+} system with different concentrations of Cu^{2+} ions.

The reason for the quenching of the photoluminescence intensity with increasing Cu^{2+} ion concentration (more than $1 \cdot 10^{-5}$ mol/l) is the decrease in the number of non-radiative centers. The emission maximum shifts from 2.46 eV (CdS/L-Cys) to 2.65 eV at the maximum concentration of Copper ions. On the other hand, at a concentration of impurity copper ions of $1 \cdot 10^{-5}$ mol/l, an increase in the intensity of photoluminescence compared to the initial Cadmium Sulfide solution by 1.25 times and a shift of the photoluminescence maximum to the short-wavelength region are observed only under the condition of synthesis according to scheme 1 (ion exchange).

Unlike the results in [15], in the optical absorption and photoluminescence spectra (Fig. 1), no additional peaks are visualized in the spectral region, but the shape of the spectral curve has changed.

2.2. Study of the optical properties of the Cu^{2+}/CdS/L-Cys/ colloidal solution obtained by coprecipitation

Changing the order of introduction of copper ions into the studied system (co-precipitation method) causes more significant changes in the optical parameters of the solution (Table 2, Fig. 2) compared to the previous case.

Synthesis of CdS NPs in the presence of Cu^{2+} ions at a concentration of $1 \cdot 10^{-5}$ mol/dm^3 stimulates the formation of larger particles than in the case of pure CdS/L-Cys, but further increase in the impurity concentration, on the contrary, inhibits particle growth. The absorption edge in all cases of introduction of Cu^{2+} ion impurities shifts to the region of larger wavelength values (Fig.2, a).

The absorption maximum is observed in the region of 3.18-3.23 eV, depending on the concentration of Copper ions. At a minimum concentration of introduced impurity Copper ions, the absorption maximum shifts to the region of lower energies, and a further increase in the concentration of copper ions causes a shift to the region of higher energies. This can be explained by the fact that copper cations at a concentration of more than $1 \cdot 10^{-5}$ mol/dm^3 are more easily incorporated into the structure of Cadmium Sulfide nanoparticles during their growth, while at lower concentrations of impurity Copper ions, such an effect is not observed.

Under the condition of coprecipitation (scheme 2), at all concentrations of the impurity component of Copper ions, quenching of the fluorescence intensity is observed (Fig. 2, b), caused by surface defects associated with the passivation of radiative centers on the surface of Cadmium Sulfide nanocrystals.

Similar patterns in the change in photoluminescence intensity are observed in [16], but for CdS:Cu nanocrystals synthesized in polymer matrices.

Since evidence of deposition of copper sulfide NPs was not observed in both types of optical spectra, the reason for the difference as a result of different doping methods should be sought in the structure of the formed NPs.

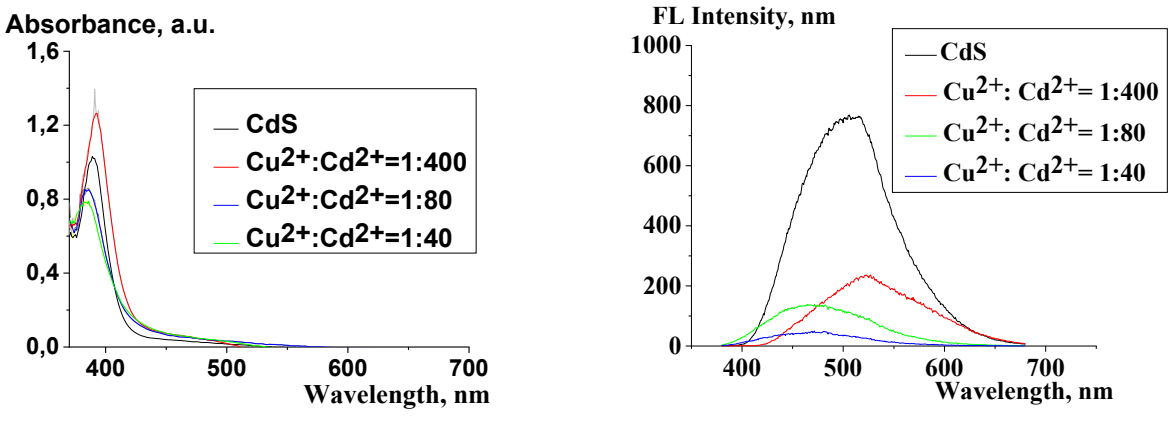
It is possible that during co-deposition, Copper ions that are isovalent to cadmium ions are introduced into the semiconductor lattice with the formation of double sulfide NPs $Cd_{1-x}Cu_xS$. When Cu^{2+} ions are added to stabilizer-coated CdS NPs, Copper ions form an outer shell in the form of CuS with the possible formation of a core/shell heterostructure.

Table 2.

Effect of $[Cu^{2+}]$ on the optical properties of the system (Cu^{2+}+ Cd^{2+})S/L-Cys(series 2)

№	$[Cu^{2+}]$, mol/l	$[Cd^{2+}]/[Cu^{2+}]$	λ_{lim} nm	λ_{max} nm	$\lambda_{max.lum}$ nm	Stokeslandslide, nm	E_g, eV
1	0	-	409	389	506	117	3,04
2	$1 \cdot 10^{-5}$	400	421	392	523	131	2,96
3	$5 \cdot 10^{-5}$	80	416	385	467	81	2,99
4	$1 \cdot 10^{-4}$	40	417	384	470	86	2,98

Note: λ_{lim} - optical absorption edge, λ_{max} - optical absorption maximum, $\lambda_{max.lum}$ - luminescence maximum, Eg – bandgap.



a b

Fig. 2. Optical absorption spectra (a) and luminescence (b) for the Cu^{2+}/CdS/L-Cys system.

Conclusions

Based on the results of this study, the following conclusions can be drawn:

By changing the concentration and order of introduction of Copper (II) cations, the optical characteristics of CdS nanoparticles stabilized with the amino acid L-Cystein can be influenced.

A limiting concentration of Cu^{2+} ions ($1 \cdot 10^{-5}$ mol/l) was established, the introduction of which into the CdS/L-Cys colloidal solution does not cause aggregation of nanoparticles and noticeably affects the position of the optical transmission edge.

It is shown that the introduction of ions $[Cu^{2+}] = 1 \cdot 10^{-5}$ mol/l after the synthesis of colloidal solutions of CdS/L-Cys (ion exchange method) increases the intensity of photoluminescence, and the maximum of photoluminescence shifts to the region of higher energies relative to the values of the initial solution of CdS/L-Cysteine NPs.

When Cu^{2+} ions are introduced during the synthesis of Cadmium Sulfide (co-precipitation), the absorption edge shifts to the long-wavelength region, the particle size increases, and the intensity of the photoluminescence spectra, the photoluminescence maximum, and the Stokes shift decrease.

Acknowledgements

The work was carried out within the framework of the scientific research topic "Study of chemical, physicochemical properties and biological activity of natural and synthetic organic compounds and compositions" (2025-2029, state registration number: 0125U001979).

Viktoriia Pylypko and Yuriy Khalavka's contribution was supported by a grant from the Simons Foundation (FI-PD-Ukraine-0001457) and partially supported by the Ministry of Science and Education of Ukraine (grant 0123U100858).

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Вплив йонів Cu^{2+} на оптичні властивості колоїдних розчинів CdS/L-Cys

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У роботі проведено дослідження по впливу йонів купруму (II) на оптичні властивості колоїдних розчинів наночастинок кадмій сульфіду стабілізованих L-Цистеїном у водному розчині за кімнатної температури 25^0C. Введення йонів Cu^{2+} проводили за методом співосадження та йонного обміну. Встановлено, що додавання розчинів солей купруму (II) різних концентрацій до колоїдних розчинів наночастинок CdS, викликає агломерацію та відповідно, зміщення краю оптичного поглинання у довгохвильову область, збільшення ширини забороненої зони кадмій сульфіду, зменшення інтенсивності фотолюмінесценції, окрім розчину із концентрацією йонів купруму (II) - $1 \cdot 10^{-5}$ моль/л .

Ключові слова: наночастинки, колоїдні розчини, гетероструктури, оптичні властивості, фотолюмінесценція.