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**NEW PHOTOCATALYTICAL SYSTEMS BASED ON TiO<sub>2</sub> AND THE SYMMETRIC  
CATIONIC POLYMETHINE DYE**

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Light-sensitive materials with some photocatalytic activity based on semiconductors are known as important functional materials since they can be employed in construction of photocatalytical systems for accumulation and transformation of solar energy, toxic waste decontamination, development of nontraditional low-tonnage syntheses of important compounds and so on.

In this context, many efforts have been made to ensure sensitization of the wide-zone semiconductors such as TiO<sub>2</sub> in order to shift their 'red' limit of the sensitivity band towards longer waves. Unfortunately, the quantum yield and overall efficiency of the phototransformations are still too low for practical realization of these solutions. That is why it is still quite topical to conduct a search for new highly effective functional materials with advanced parameters. As proved by numerous investigations performed before, the heterostructure made of a semiconductor, the dye-sensitizer and the protective polymer is a promising solution to improve the operation characteristics of the photosystems.

The symmetric cationic dye was used as the semiconductor and polyepoxypropylcarbazole was used as the polymer-protector. The photoreduction of methylene blue was taken as a model process for evaluation of the heterostructures photocatalytic activity. Following the experimental method, a mixture of the Polymer/Dye/TiO<sub>2</sub> heterostructures, methylene blue and formaldehyde was irradiated at active stirring in the oxygen free atmosphere until complete discoloration of methylene blue. As was investigated the photocatalytic reduction of methylene blue can be initiated either by the light being absorbed by TiO<sub>2</sub> or because of the light absorption performed by the dye-sensitizer. However, a character of relation between photocatalytic activity and the dye content depends on the light absorption mechanism. If the process is controlled by the light absorbed by TiO<sub>2</sub>, photocatalytic activity is constantly decreasing with growth of the dye content while its initial growth then changes to a fall in case the process is controlled by another mechanism (photoexcitation of the dye).

In the view of such changes in photocatalytic activity values, one can suppose that they can be caused by sensitization of heterostructure Polymer/Dye/TiO<sub>2</sub> to the visible light, which cannot be absorbed by the pure titania. It is obvious that the growth of dye content in heterostructure would result in a better light absorbance and, consequently, a higher activity of heterostructure. Next decrease in the photocatalytic activity value at further growth of dye content can be resulted by weakening of interaction between the dye and the substrate that occurs at some higher contents of dye and puts obstacles on the interphase electron transfer. Besides, same effect can also be caused by formation of the less light-sensitive associates at the increased content of the dye.

It can be concluded that the results of this investigation prove that the symmetric cationic dye is capable of acting as a sensitizer of titanium dioxide. The dye's light sensitivity zones and its excited redox potentials were determined. It was shown that their potentials were sufficient to realize the sensitization of TiO<sub>2</sub> by electrons transfer to its conductivity zone.

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**STATISTICA (STATSOFT) PROGRAM IN EXPERIMENT PLANNING AND  
VISUALIZATION OF THE CONTENT-PROPERTY DEPENDENCY IN THE SYSTEM  
Cd<sup>2+</sup>-L-CYSTEINE-S<sup>2-</sup>**

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The aim of the work: to investigate the effect of precursor concentration in the three-component system Cd<sup>2+</sup>- L-Cys - S<sup>2-</sup> on the optical properties of the resulting nanoparticles of cadmium sulfide stabilized by the amino acid L-Cysteine, using the Statistica program.

Objective: to conduct a number of experiments on the synthesis and research of optical properties of IC CdS/L-Cys according to the planning of the program Statistica selected version of the program Ternary Plans, 3D (Mixture designs).

Materials and methods: initial reagents of high qualification: 0.5 M solution  $\text{CdCl}_2 \cdot 2,5\text{H}_2\text{O}$  "x.h." 0.05 M solution L-Cysteine ( $\text{HOOC-CH}(\text{NH}_2)\text{-CH}_2\text{-SH}$ ) "h.h."; 0.5 M  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  solution (99% Aldrich purity), 0.1 M NaOH solution. The study of optical properties of solutions was carried out at a temperature of  $298 \pm 5$  K using spectrophotometers MDR-4 and USB-650 (Ocean Optics). The optical density of solutions was measured within the values of 0.01 – 2 with an increase in the wavelength in the range of 350 – 1000 nm.

The STATISTICA program covers a large number of statistical analysis methods (more than 250 built-in functions) combined with specialized statistical modules that provide advanced interactive visualization tools. Ternary Plot, 3D (Mixture designs) is selected to construct a mathematical model of the "composition-property" dependency of the three-component  $\text{Cd}^{2+}$  – L-Cys –  $\text{S}^{2-}$  system. The non-monotonous effect of the content of each precursor on the optical characteristics of stabilized colloidal solutions of IC illustrates the three-dimensional (according to the STATISTICA program) graphical interpretation of the obtained data and its projection on the plane is shown in Fig. The complete cubic equation for describing isolum absorption edge is:

$$= 435 x_1 + 434 x_2 + 445 x_3 - 81 x_1 x_2 + 16 x_1 x_3 - 10 x_2 x_3 + 55 x_1 x_2 (x_1 - x_2) + 124 x_1 x_3 (x_1 - x_3) + 106 x_2 x_3 (x_2 - x_3) - 350 x_1 x_2 x_3 .$$

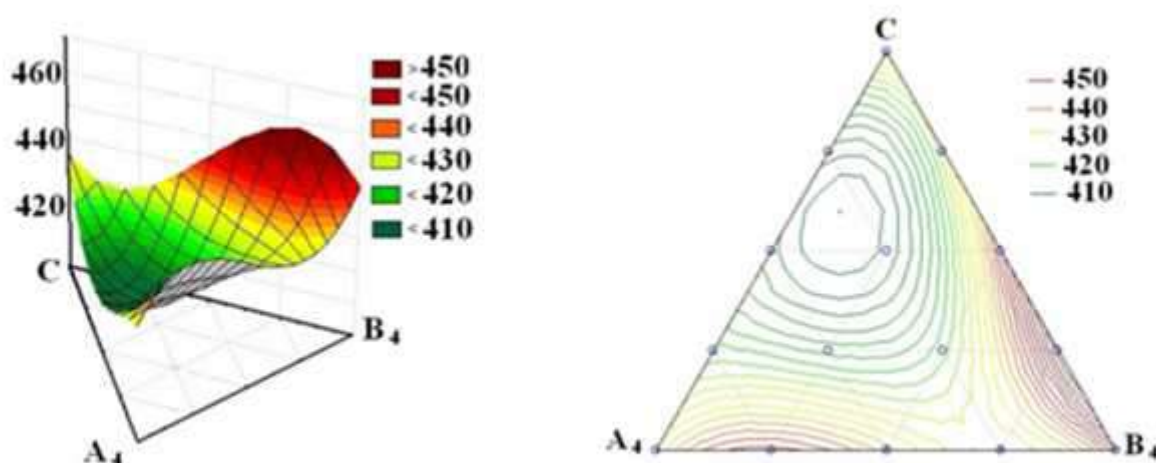


Fig. 3D-image of concentration dependence of the absorption edge of the studied solutions of the  $\text{Cd}^{2+}$  – L-Cys –  $\text{S}^{2-}$  system (left) and its projection to the plane (right), summarized by the complete cubic equation.

Thus, statistical processing of the results obtained equation and built diagrams of concentration dependencies of wavelengths of the edge of optical absorption of colloidal solutions of semiconductor nanoparticles CdS in system  $\text{Cd}^{2+}$  – L-Cys –  $\text{S}^{2-}$  under condition of pH synthesis = 11,  $T = 298 \pm 2$  K. Based on the research carried out using the program Statistica (Ternary Plot, 3D Mixture designs) the areas of time-stable colloidal solutions of CdS/L-Cys nanoparticles in the system are determined  $\text{Cd}^{2+}$  – L-Cys –  $\text{S}^{2-}$ :  $\text{Cd}^{2+}$ : 10,0 – 35,0 %;  $\text{S}^{2-}$ : 10,0 – 35,0 %; L-Cys: 30,0 – 80,0 %; and unstable: 1)  $\text{Cd}^{2+}$ : 47,5 – 60,0 %;  $\text{S}^{2-}$ : 10,0 – 22,5 %; L-Cys: 30,0 – 55,0 %; 2)  $\text{Cd}^{2+}$ : 10,0 – 22,5 %;  $\text{S}^{2-}$ : 35,0 – 60,0 %; L-Cys: 30,0 – 55,0 %.