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The Photophysical Properties Investigation of Hybrid Associates of Methylene Blue Molecules with Colloidal CdS Quantum Dots and CdS / Cd(OH)$_2$ "Core-Shell" Systems

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The spectral properties of associates of methylene blue molecules with colloidal CdS quantum dots and CdS / Cd(OH)$_2$ «core-shell» systems were investigated. It is shown that according to environment methylene blue changes its photophysical properties during association. These properties are due to changes of MB structure as a result of oxidation-reduction reactions.

Keywords: CdS quantum dot, Methylene blue, Hybrid associates, Luminescence.

1. INTRODUCTION

Today various objects of nanotechnology are very interesting. Particularly, hybrid systems, composed of semiconductor quantum dots (QDs) and biologically active molecules, are interesting. It is due to large range of potential applications, including photocatalysts, the components of photovoltaic devices, biological and medical chips, etc. [1-3].

Now, colloidal quantum dots (CdSe, CdTe, ZnSe, etc.) and their associates with molecules of porphyrins, phthalocyanines, thiazines and ect. are used as a model hybrid nanostructures for various kinds of medical and biological applications [4-6].

One of the most perspective materials for constructing of hybrid associates is thiazine methylene blue (MB) dye. Its properties let to use it for various applications, including chemical indicators, markers and spectral sensitization systems for photovoltaic and photocatalysis elements [1-3].

However, hybrid associates based on CdSe, CdTe, ZnSe QDs are very toxic. The conditions of them organo-metallic synthesis are toxic too. Therefore they are inapplicable in vivo. They can only be used for laboratory fluorescent diagnostics of biopsy material. One of this problem solution is to build-up of nontoxic shell on the luminescent core.

On the one hand, the formation of the sell leads to a decrease of toxicity and increase of luminescence intensity. This is due to decrease of concentration of dangling bonds on the QDs interface. Those bonds are nonradiative recombination centers [7]. On the other hand, the shell blocks direct contact of dye molecules with QD. The variation of its thickness provides possibility for evidence primary mechanism of electron excitation interchange between components of associates. However, such manipulations transform the character of interaction thought "middleman" of associates components. Transformation of dye molecule structure is possible during hybrid association.

In this paper we analyzed the spectral properties of hybrid associates of methylene blue with colloidal CdS QDs, having variously composition of the interface part. In particular, we consider the situation when the conjugation of MB molecules was realized with growing and pre-formed surface CdS QDs, as well as in the conditions of systems of CdS / Cd(OH)$_2$ «core-shell», obtained by sol-gel method in gelatin matrix [8].

2. EXPERIMENTAL SECTION

2.1 Investigated Samples

Gelatin-stabilised CdS QD samples were prepared by the sol-gel method [8]. QDs were synthesised by the double jet confluence of aqueous solutions of CdBr$_2$ and Na$_2$S with a gelatin solution in a reactor at a constant temperature of 40 °C and a constant pH = 7. An inert alkaline photographic gelatin solution (3 %) was used.

Preparation of a mixture of CdS QDs with MB molecule was realized in two ways [8]. In one case, aqueous solution of MB with the required concentration was introduced into the melt of the gelatin sol during the final stage of CdS QD growth. In the other case, mixing of MB molecules was produced with already formed CdS QDs. The first method provides interaction of MB molecules with growing surface of CdS QDs, and the second provides it with already formed surface. The reactivity of CdS QDs surface in these different conditions must have different surface composition and its donor-acceptor properties.

The "core-shell" systems were obtained by build up of sell on colloidal CdS QDs, obtained by sol-gel method. Detailed description of the preparation technique is given in [8]. The CdS / Cd(OH)$_2$ shell was prepared by slow injection of aqueous solutions of NaOH and CdBr$_2$ in gelatin sol, formed colloidal CdS QDs. The quantity of introduced reagents was calculated taking into account the receipt of a two-monolayers coatings of QDs surface by shell. In this case the MB aqueous solution

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was injected into gelatin sol formed CdS / Cd(OH)$_2$ «core-shell» systems.

High purity crystal hydrates of MB, given by Sigma-Aldrich company were used for the preparation of MB aqueous solutions. MB was added to a $10^{-3} \div 10^{-2}$ mole of dye / mole of CdS QDs concentrations (mol fraction or m.f.). At maximal concentrations of MB 4 molecules of the dye fit one QD had a diameter of 2.5-2.7 nm. The preparing mixture was applied to a quartz plate.

The identification of colloidal CdS QDs was made using a transmission electron microscope (TEM) LEO ~ 912AB ~ OMEGA. Analysis of the electron micrographs shows that isolated CdS nanoparticles with average size of 2.5 nm are formed. When core of CdS QDs was covered by shell with thickness of up to two monolayers we observed an increase in the average size. It is about 1.2 nm. The reverse electron scattering analysis showed that the crystallization of CdS QDs are in a cubic lattice.

2.2 Methods of Investigations and Equipment

The investigations were performed with the use of luminescence and absorption techniques. The absorption and luminescence spectra of prepared samples were investigated using the absorption spectrophotometer Shimadzu UV 2501 (Japan) and fully automatic spectral-luminescent complex. This complex was built on the basis of the diffraction monochromator and photomultiplier (R928P Hamamatsu, Japan, battery energy source C4900-51), operating in the photon counting mode. Luminescence of samples was excited by UV radiation produced by an HPL-H77GV1BT-V1 diode module ($\lambda_{max} = 380$ nm, $P_{max} = 5$ mW). The presented results were obtained at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows the normalized absorption spectra of MB in variously environment.

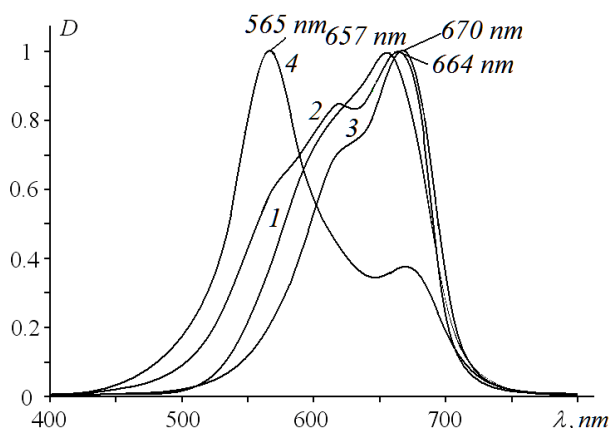The following main regularities were identified in these spectra:

Fig. 1 – Normalized absorption spectra of MB (10-2 m.f.) in variously environment. 1 – mixture with CdS QDs (conjugation with growing QD surface); 2 – mixture with CdS QDs (conjugation with formed QD surface); 3 – mixture with CdS / Cd(OH)$_2$ (1 monolayer); 4 – mixture with CdS / Cd(OH)$_2$ (3 monolayer)

• For MB, conjugated with the growing surface of colloidal CdS QDs maximum absorption is hypsochromically shifted with respect to the main peak of MB spectrum in gelatin ($\lambda_{max} = 664$ nm) to 10 nm (Fig. 1(1)).

• The absorption spectrum of MB molecules, conjugated with formed surface of CdS QDs has band at $\lambda_{max}^1 = 664$ nm and $\lambda_{max}^2 = 613$ nm and feature at 570-580 nm (Fig. 1(2)). This spectrum is close to the spectrum of MB in the gelatin.

• The absorption spectrum of a mixture of MB molecules with CdS / Cd(OH)$_2$ QDs, having the shell thickness no more than a monolayer, has a pronounced maximum at $\lambda_{max}^1 = 670$ nm (Fig. 1(3)) and the feature at the absorption band of MB dimers (610-615 nm). When Cd(OH)$_2$ sell thickness is increase to 2-3 monolayers there is another band with $\lambda_{max}^3 = 565$ nm (Fig. 1(4)). The absorption band intensity of the monomers and dimers of MB is decreases.

Luminescent properties of hybrid associates of CdS QDs and Cd(OH)$_2$ «core-sell» systems with MB molecules in the gelatin were investigated using excitation radiation with wavelengths $\lambda_{ex} = 380$ nm. It occurs in the region of excitation emission of QDs.

In photoluminescence spectra excited by $\lambda_{ex} = 380$ nm, it was found that the CdS QDs fluoresce is brightly enough. Maximum of luminescence is located at 540-550 nm (Fig. 2(1)).

In the presence of MB molecules luminescent properties of CdS QDs are undergoing significant changes. The luminescence band was recorded in the long-wavelength part of the spectrum. Its maximum for mixtures of MB molecules with growing surface of colloidal CdS QDs is located at 681 nm (Fig. 2(1)). In the case of formed QDs surface long-wavelength maximum of luminescence was located at 674 nm (Fig. 2(1")). Moreover, for all types of associations we had the same pattern. It is the luminescence quenching in the QD band and a significant increase in the fluorescence of MB in the region of $674 \div 684$ nm.
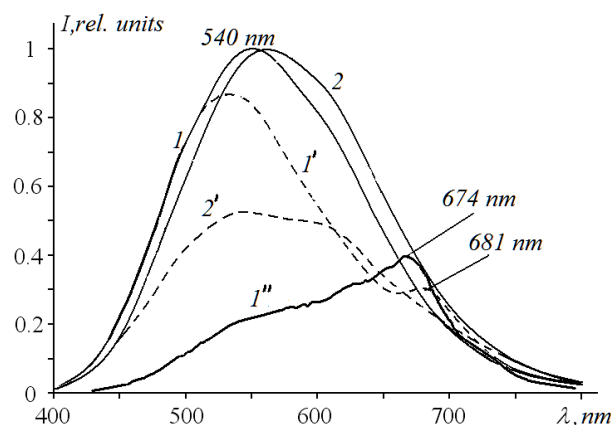

Fig. 2 – Luminescence spectra of QDs and hybrid associates with MB (10-2 m.f.). 1 – CdS QDs; 1' – mixture with CdS QDs (conjugation with growing QD surface); 1" – mixture with CdS QDs (conjugation with formed QD surface); 2 – CdS / Cd(OH)$_2$ (3 monolayer); 2' – mixture with CdS / Cd(OH)$_2$ (3 monolayer)

For "core-shell" systems the maximum of luminescence spectrum is shifted to longer wavelengths range as compared with QDs without sell (Fig. 2 (2, 3)). When MB

molecules were conjugated with CdS / Cd(OH)$_2$ «core-shell» (2-3 monolayer) the noticeable deformation of the luminescence band and minor dip in the region 560-600 nm were detected (Fig. 2(2)). This region corresponds to absorption range of the dye conjugated with the CdS / Cd(OH)$_2$ "core-shell». In the luminescence spectrum maxima at 610 nm and 697 nm were shown up.

First of all the resulting spectral features indicate the manifestation of general regularities. It is interaction and formation of every hybrid associates of QDs with MB molecules. The environmental conditions influence significant on the spectral properties of associates. Namely it is the state of surface.

The observed regularities can be explained by complex structures of MB molecules, which is characterized by a variety protolytic equilibrium. The neutral leuco-form MBH^0 occurs as a result of the reaction MB$^+$ + 2e + H$^+$ → MBH^0 in the presence of ions of variable valence metals at pH = 2 ÷ 7 [9]. It is clear in the visible and near IR regions [9]. MBH^{2+} occurs in strongly acidic environments (pH < 0.1) [10]. The protonated dication MBH^{2+} has a complex absorption band ($\lambda_1 = 741$-745 nm, $\lambda_2 = 678$ nm and $\lambda_{(3)shoulder} = 615$ nm) [11]. Today there isn't clear concept of what happens with MB molecule in a strongly alkaline environment. The cation MB$^+$ accepts an electron in strongly alkaline environments (pH > 11). Additionally, the neutral semiquinone (radical) MB^0 is observed under these conditions. This form is interesting because it has an extended absorption spectrum with five peaks in the visible region ($\lambda_1 = 420$ nm, $\lambda_2 = 436$ nm, $\lambda_3 = 585$ nm, $\lambda_4 = 610$ nm, $\lambda_5 = 640$ nm) [11, 12]. At the same time, the protonated form of MB$^+$ have a band with maximum located at 510-550 nm in different solvents [12]. This form is stable to external influence. According to [13], in strongly alkaline environment there is absorption of light at 560-575 nm by hydroxide form of methylene blue [MB] OH$^-$. In addition, there is another point of view. The dye is not simply goes over to the other form, and methylene violet dye forms [14]. The transformation into a new dye does not occur immediately. In process of time under light the transformation occurs with the possible formation of intermediate dye (Azure A, Azure B, Azure C). Transformation into methylene violet is occurred by demitiloaminogroups hydrolysis. The wide band in the region of 470-580 nm is observed [14].

The following conclusions were made considering above:

1. In the case of growing surface of CdS QDs associates with cation-radical MB$^+$ are formed. The nature of the interaction is such that it prevents to form dimers [MV$^+$]$_2$ and H-aggregates. Hypsochromically shifted to 630-655 nm absorption band may belong to this form. The nature of hypsochromicall shift in the electronic band is caused by a change in the chain length of π-conjugation. It is due to the dimensional deformation of molecules interacting with the surface, which has a spherical curvature.

2. It was found spectrally that the structure of MB molecule is transformed during conjugation with a CdS / Cd(OH)$_2$ system. Transformation can take place in two ways. The first way is the formation of MB-OH· structure during conjugation with CdS / Cd(OH)$_2$ [13]. Second is the formation of a methylene violet dye [14]. When Cd(OH)$_2$ shell is build up there are an excessive amount of OH-ions on the surface. The interaction of OH group with the nitrogen atom in heterocycle leads to N-hydroxistructure formation of MB [15]. Non-reversible changes in methylene violet are possible during the transfer of electron to environment [16].

3. For mixtures MB with formed surface of CDS QDs we observed absorption at $\lambda_{max}^1 = $ maxima at 664 nm and $\lambda_{max}^2 = 613$ nm, and the feature at 570 nm. Transformation of this feature in separate band during increasing thickness of the shell to 2-3 monolayers suggests that this feature is due to the formation of same dye forms as in the case of Cd(OH)$_2$ shell. The hydrolysis of dangling bonds is possible for formed CdS QDs surface. As its result pH of sol is shifted to alkali. Thereby, similar situations as for CdS / Cd(OH)$_2$ «core-shell » are possible during adsorption of MB on surface. Definitely to say what is a degradation product of MB for these cases is not possible. Both schemes are possible. Interaction with highly reactive QDs surface can plays decisive role in the formation of associates of MB with formed surface of CdS QDs and CdS / Cd(OH)$_2$.

4. Analysis of luminescence spectra of hybrid associates of MB shows that for them the change in shape of luminescence spectrum is situated in agreement with the changes observed in absorption spectra. Principal detected feature is the increase of luminescence intensity of MB and its decrease for QDs. Comparison of luminescence spectra of CdS QDs and CdS / Cd(OH)$_2$ systems with MB absorption indicates that they significantly overlap. This can be regarded as the spectral correspondence of resonance conditions for the transfer of electron excitation energy from CdS QDs to MB.

4. CONCLUSION

Thus, MB exhibits different spectral properties in associate. Its properties are dependence from the environment. In hybrid associates of MB with CdS QDs in the case of growing surface dye is present mainly as MB$^+$. In hybrid associates of MB with CdS QDs in conditions of formed surface and CdS / Cd(OH)$_2$ systems the conjugation is due to interaction of the dye with the interface part of QDs. It is determined by charged surface, presence of gelatin and hydrolysis of the dangling bonds on the surface of CdS QDs. The hydrolysis provides the formation of new dye forms. They are MB^{0}OH and methylene violet. Transformation forms of methylene blue in the studied hybrid associates fully explains their spectral luminescent properties.

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