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# Luminescence properties of hydrophilic hybrid associates of colloidal CdS quantum dots and methylene blue

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## ABSTRACT

Luminescence properties of hybrid associates of semiconductor colloidal CdS quantum dots (QDs) with an average diameter of 2.5 nm and methylene blue (MB<sup>+</sup>) cations were investigated. Their photo-luminescence spectra, excitation spectra and luminescence decay spectra recorded using the time-correlated single photon counting techniques were analyzed. The increase of efficiency of MB<sup>+</sup> fluorescence at 405 nm excitation was found. It corresponds to the absorption region of CdS QDs. When  $[n_{\text{CdS QDs}}] : [n_{\text{MB}^+}]$  concentrations ratio changes from 100:1 to 1:3 for associates, then a decrease in the intensity of CdS QDs luminescence band (580 nm) and its increase for MB<sup>+</sup> band (674 nm) were observed. At the same time it was found that the average lifetime of CdS QDs luminescence is shortened and the lifetime of MB<sup>+</sup> luminescence becomes significantly longer. It was concluded that dynamic quenching due to nonradiative resonance energy transfer takes place. The efficiency of this process was estimated and the corresponding rate constant was calculated. It is  $5.6 \times 10^7$  to  $8.6 \times 10^7$  s<sup>-1</sup>.

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## 1. Introduction

Ultrasmall sizes and unique physical properties of colloidal semiconductor quantum dots (QDs) (high brightness of luminescence, photostability, wide excitation range, the size-dependent optical properties) make them ideal for various applications of science, technics and medical technology [1–9]. One of the most actively developing areas is making biological labels, sensors and sensitizers for photodynamic therapy (PDT) of cancer [1,3,6–9]. Hybrid associates of good luminescence colloidal QDs and biologically active molecules (QD–Dye) are most interesting for PDT [6–20]. Hybrid associates of QDs with organic dyes are particularly interesting. These dyes should have a high triplet yield and energy structure, appropriate for photosensitization of  $^3\text{O}_2 \rightarrow ^1\text{O}_2$  process (porphyrins, phthalocyanines of metal, thiazine dyes, etc. [8,9,12–20]). In particular, associates of QDs with methylene blue (MB) molecules are interesting due to unique properties of MB<sup>+</sup> cation [3,9,19,20]. The low location of triplet state, high yield of inter-system crossing and efficiency of  $^3\text{O}_2 \rightarrow ^1\text{O}_2$  process photosensitization are characteristic of MB<sup>+</sup>. Besides, the formation of QD–MB<sup>+</sup> associates allows the dye to stay in the form of MB<sup>+</sup> cation for a long time [3]. This is extremely important because MB<sup>+</sup> is capable of aggregation and transformation into various proteolytic

forms. These forms are incapable of  $^3\text{O}_2 \rightarrow ^1\text{O}_2$  process photosensitization [3,19].

Usually in QD–Dye hybrid associates photoexcited QDs act as donors. Dye molecules in QD–Dye hybrid associates act as acceptors of electron excitation. The main ways of excitation transfer are non-radiative (Förster) resonance energy transfer (FRET) [3,10,13–20], photoinduced electron transfer (PET) [3,12], luminescence resonance energy transfer (LRET), based on the reabsorption of donor luminescence (QDs) by the acceptor (Dye) [11]. The choice of the dominant channel for electron excitation exchange in QD–Dye hybrid associates requires a detailed justification in each case. One of the most difficult and demanding investigations is resonance nonradiative energy transfer. Universal criteria for the choice of the appropriate model are necessary for detailing the mechanism of this process in each particular case. Their formulation requires the analysis of the broadest possible spectrum of empirical regularities for different types of associates.

It is necessary to note that when an associate includes QDs, having a luminescence peak with a large Stokes shift, quenching of QDs luminescence and increase in intensity of Dye luminescence are observed [17]. However, conditions of resonance for electron excitation exchange must be corrected. They should be different from the case where the associate includes QDs with dominant radiative annihilation of free excitons [3].

Thus, experimental studies of resonance energy transfer processes are relevant for a wide range of associates synthesized not

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only with high-temperature organometallic synthesis, but also with significantly lower-temperature methods, such as the sol–gel method. The advantage of the latter approach is the possibility to provide low toxicity of synthesis conditions of hydrophilic QDs, their bright recombination luminescence and direct contact of QDs with Dyes. Research in this way will make steps to the formation of a unified view about the problem of resonance energy transfer in QD–Dye hybrid associates.

In this paper we report the results of studies of luminescence properties of hydrophilic hybrid associates of colloidal semiconductor CdS QDs with an average diameter of 2.5 nm and MB<sup>+</sup> cations. Presented data sufficiently detail results of the spectroscopic study of the hybrid association of CdS QDs and MB<sup>+</sup> cations in a gelatin matrix [21,22]. They are focused on the detail of process of electronic excitation exchange in QD–MB<sup>+</sup> associates, using, primarily, fluorescence lifetime measurements.

## 2. Material and methods

### 2.1. Investigated samples

The synthesis of colloidal CdS QDs in gelatin and their conjugation with MB<sup>+</sup> molecules were realized within sol–gel technique. Detailed description of the preparation technique is given in Refs. [21,22]. The method consists of mixing of  $1.3 \times 10^{-3}$  M CdBr<sub>2</sub> × 2.5 H<sub>2</sub>O and  $1.3 \times 10^{-3}$  M Na<sub>2</sub>S × 9 H<sub>2</sub>O dissolved in 50 ml of bidistilled water into a reactor containing 200 ml of bidistilled water and 6 g of inert gelatin. Mixing was realized under continuous agitation by magnetic stirring at a speed of 300 rpm. The temperature in reactor during the synthesis was 60 °C. The QDs growth in reactor was limited by stopping chemical reaction. QD–MB<sup>+</sup> associates were obtained by mixing solutions containing gelatin sol of QDs and MB<sup>+</sup> with certain concentration. The hybrid association was realized during the final stage of CdS QDs interface formation. This provided direct contact of CdS QDs and MB<sup>+</sup> molecules. The concentrations of MB<sup>+</sup> were  $10^{-3}$ – $10^{-1}$  moles of dye/mole of CdS QDs (mole fraction or m.f.). This MB<sup>+</sup> concentration range provides variation of [n<sub>CdS QDs</sub>]:[n<sub>MB<sup>+</sup></sub>] concentrations ratio from 100:1 to 1:3. This ratio was unlimited by dimers and H-aggregates formation, which takes place for a large concentration of MB<sup>+</sup> [23]. Used MB molecules had high purity and were obtained from Sigma-Aldrich. They are produced as MB hydrates (C<sub>16</sub>H<sub>18</sub>ClN<sub>3</sub>S\*3H<sub>2</sub>O). For further research obtained aqueous-gelatin sols of QD–MB<sup>+</sup> associates were applied to quartz plates (2 × 2 cm) and dried.

### 2.2. Methods of investigation and equipment

UV–vis absorption spectra of CdS QDs, MB and their mixtures were recorded using a Shimadzu BioSpec-mini (Japan) spectrophotometer.

The photoluminescence (PL) and its lifetime were measured using Ocean Optics Maya~Pro 2000 and PicoQuant Time-Harp~100 TCSPC system. PL and its decay were measured using the PicoQuant PDL 800-B semiconductor pulsed laser with a wavelength of 405 nm and a pulse length of 75 ps and repetition 100 kHz. Luminescence excitation spectra were recorded using fluorescence spectrometer LS 45 Perkin Elmer.

Transmission electron micrograph (TEM) images were obtained with an LEO~912 AB~OMEGA microscope.

The crystal structure of synthesized QDs was investigated with X-ray diffractometer ARL X'TRA (Switzerland) for K<sub>α1</sub> of copper.

## 3. Results and discussion

### 3.1. Structure and spectral characteristics

TEM and XRD pattern data agrees with preliminary studies [22]. Using the technique of synthesis allowed us to obtain colloidal CdS QDs. Analysis of TEM images (Fig. 1) showed that QDs with an average size of  $2.5 \pm 0.4$  nm are formed.

XRD pattern shows that QDs are crystallized in the cubic phase (Fig. 2).

The average diameter found from TEM images analysis was confirmed by the estimation of size using Scherrer's equation from the half-width of XRD reflexes

$$d = \frac{0.89\lambda}{\beta \cos \theta_B} \quad (1)$$

$d$  is the average diameter of nanoparticles,  $\lambda$  is the K<sub>α1</sub> Cu wavelength (1.5405 Å) radiation,  $\beta$  (in radians) is the full width at half maximum,  $\theta_B$  is Bragg's angle.

### 3.2. UV–vis absorption spectra

Fig. 3 shows UV–vis absorption spectra of QD–MB<sup>+</sup> mixtures and their components recorded in the region of 250–800 nm. The absorption spectrum of CdS QDs has a pronounced exciton peak at

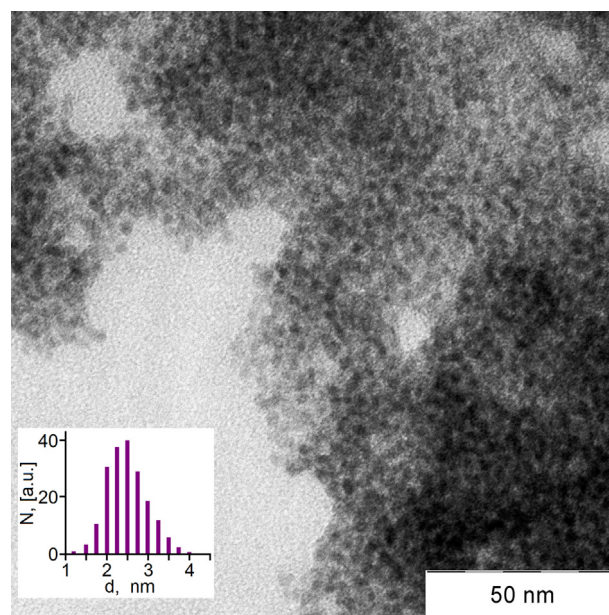


Fig. 1. Size distribution and TEM images of CdS QDs.

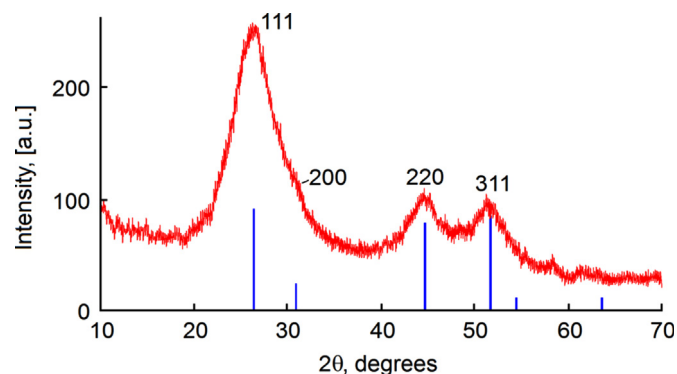


Fig. 2. XRD pattern of CdS QDs.

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