

# Singlet oxygen luminescence detecting in presence of hybrid associates of colloidal Ag<sub>2</sub>S quantum dots with methylene blue molecules

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**Abstract.** In our work we demonstrate some spectroscopic investigation of colloidal Ag<sub>2</sub>S QDs associates with methylene blue. The photosensitizing of singlet oxygen by associates of colloidal Ag<sub>2</sub>S QDs with methylene blue was found.

Colloidal Ag<sub>2</sub>S quantum dots (QDs) are promising material for fluorescent labeling of biological objects, including tissues affected by severe diseases. It is possible due to their intense IR luminescence. Luminescence in the region of 800-1200 nm corresponds to the therapeutic window of transparency of biological objects [1-3]. Hybrid association of Ag<sub>2</sub>S QDs with molecules of thiazine dyes opens additional possibilities to control the quantum yield of QDs luminescence [3], and also to photosensitize singlet oxygen (<sup>1</sup>O<sub>2</sub>). This is interesting for photodynamic therapy, particularly in combination with high-contrast fluorescent marking [4,5]. Furthermore, conjugation of QDs with dye molecules can to provide higher stability of dye, for example, methylene blue (MB) in the form, which produces singlet oxygen [6].

There is a problem of unambiguous fluorescent detection of singlet oxygen in the region of 1270 nm due to Ag<sub>2</sub>S QDs luminescence with peak at 1200 nm for most of known methods of their synthesis. This problem is also deepened due to significant duration of luminescence decay of Ag<sub>2</sub>S QDs, which is overlapped with kinetics of luminescence of singlet oxygen. Therefore we solved the problem of changing the position of IR luminescence peak of Ag<sub>2</sub>S QDs. This peak has weak size dependence. Its position was changed by replacing of stabilizer. Colloidal Ag<sub>2</sub>S QDs were synthesized in aqueous gelatin solution and using thioglycolic acid (TGA).

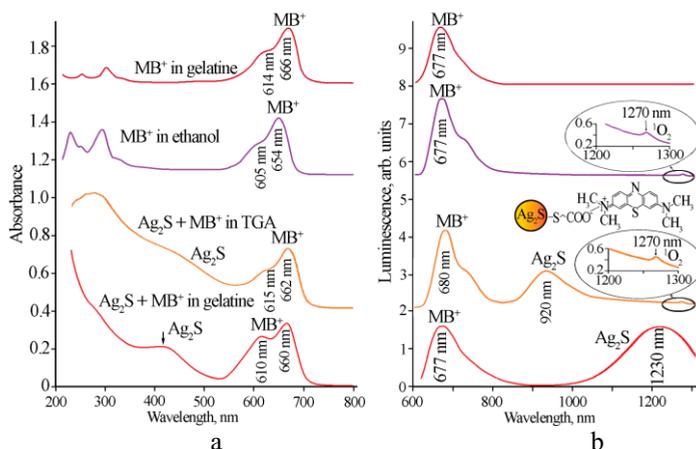
The possibility of singlet oxygen photosensitization in water-ethanol solutions of mixtures of colloidal semiconductor Ag<sub>2</sub>S QDs, conjugated with MB molecules was investigated for synthesized samples. We used colloidal semiconductor Ag<sub>2</sub>S QDs with average size of 2.2 – 3.0 nm and MB molecules with concentration, provided QDs:MB=1:3 and QDs:MB=1:8 ratio respectively.

Detection of singlet oxygen production was realized using a technique, based on the measurement of <sup>1</sup>O<sub>2</sub> molecules phosphorescence at 1270 nm. Registration of <sup>1</sup>O<sub>2</sub> molecules phosphorescence was realized using a highly stable low-noise photodiode PDF-10C/M and

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monochromator MDR-4. The excitation sources was laser diode LPC-836 ( $\lambda_{\max} = 660 \text{ nm}$ ,  $P_{\max} = 250 \text{ mW}$ ).



**Fig. 1.** UV-Vis absorption (a) and luminescence (b) spectra of MB in different solvents and mixtures of colloidal  $\text{Ag}_2\text{S}$  QDs with MB in gelatin and TGA. Insert is scheme of interaction between  $\text{Ag}_2\text{S}$  QDs and MB in TGA.

As result of investigations it was found: 1) Synthesized  $\text{Ag}_2\text{S}$  QDs in gelatin have an average size of 2.2 nm (according TEM) and 3.0 nm in TGA. The size effect is observed in UV-Vis absorption spectra (fig. 1, a). Replacement of stabilizer from gelatin to TGA provides a shift of  $\text{Ag}_2\text{S}$  QDs luminescence peak from 1230 nm to 920 nm for similar size of  $\text{Ag}_2\text{S}$  QDs (fig. 1b). This result indicates interface nature of recombinational IR luminescence of  $\text{Ag}_2\text{S}$  QDs. 2) A slight shift of peak of the order 4-5 nm is observed in UV-Vis absorption spectra of MB molecules during formation of mixtures with  $\text{Ag}_2\text{S}$  QDs. This indicates a relatively weak interaction between MB molecules and  $\text{Ag}_2\text{S}$  QDs, realized probably by dipole-dipole mechanism with involving of dimethylamino groups of MB and incomplete bonds of QDs and also stabilizer molecules (fig. 1). 3) The association leads to a redistribution of the luminescence intensity of QDs and MB molecules. In the case of mixtures of  $\text{Ag}_2\text{S}$  QDs and MB in TGA and gelatin we occur quenching of QDs luminescence under excitation from the absorption band of MB. Observed regularities are manifestation of interaction between MB molecules and  $\text{Ag}_2\text{S}$  QDs. This fact can be explained by ionization of  $\text{Ag}_2\text{S}$  QDs due to transfer of photoexcited electron to  $\text{MB}^+$ , owned acceptor properties in its triplet state. 4) Singlet oxygen photosensitization was found in ethanol solution of MB (fig 1b). The peak of singlet oxygen phosphorescence at 1270 nm was detected in photoluminescence spectra of mixtures of  $\text{Ag}_2\text{S}$  QDs and MB in TGA [5]. It is not typical for photoluminescence spectrum of pure  $\text{Ag}_2\text{S}$  QDs in TGA. To observed similar peak for mixtures  $\text{Ag}_2\text{S}$  QDs and MB in gelatin is difficult due to intense luminescence of  $\text{Ag}_2\text{S}$  QDs (1230 nm).

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## References

1. G. Honge et al., *Angew. Chem.* **124**, 9956 (2012)
2. I. Hocaoglu et al., *J. Mater. Chem.* **22**, 14674 (2012)
3. T.S. Kondratenko et al., *Technical Physics Letters* **42**, 365 (2016)
4. A. Fernandez-Fernandez et al., *Appl. Biochem. Biotechnol.* **165**, 1628 (2011)
5. S.Yu. Egorov, A.A. Krasnovsky, *Biophysika.* **28**, 497 (1983)
6. L. Li, *Chem. Commun.* **51**, 14357 (2015)