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Luminescent properties of colloidal Ag_2S quantum dots passivated with thioglycolic acid molecules in the presence of oxtetracycline

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Received October 28, 2024
Revised December 04, 2024
Accepted December 05, 2024

It was found that in the presence of oxytetracycline molecules, the spectral absorption and luminescence profiles of colloidal Ag_2S quantum dots passivated with thioglycolic acid (TGA) molecules are transformed. When mixing a colloidal solution of Ag_2S/TGA quantum dots with antibiotic molecules, a peak with a maximum at 820 nm appears in the absorption spectrum, and a shift in the luminescence maximum to the short-wave region (from 940 to 860 nm) accompanied by an increase in its intensity is observed in the luminescence spectrum. The observed regularities are due to a change in the state of the Ag_2S/TGA quantum dots interface due to binding to the oxytetracycline molecule through the interaction of the tricarbonyl group with dangling bonds on the surface of the quantum dots and passivator molecules, providing the formation of new radiative recombination centers. The obtained results indicate the possibility of practical application of a colloidal solution of Ag_2S/TGA quantum dots as a luminescent receptor for the presence of tetracycline antibiotics in solution.

Keywords: trap-state luminescence, Ag_2S quantum dots, oxytetracycline, interface.

DOI: 10.61011/EOS.2025.01.60568.7262-24

Introduction

In recent years, the development of new technologies and materials for screening the environment and food for the presence of antibiotics has been an urgent issue [1–3]. Semiconductor colloidal quantum dots (QDs) are recognized as a promising receptor in luminescent sensors, with their surface chemistry making it possible to bind to various molecules, ensuring selectivity of the sensor to the target analyte, while control of QD size helps adjusting the spectral luminescent properties over a wide spectral range [4–21].

The coupling of molecules and QDs impacts the luminescent properties of the latter and manifests itself both, as flaring/quenching of luminescence and changing the spectral contour depending on the mechanisms of interactions in the combined system. In some studies it was shown that such interaction may provide conditions for exchange of electronic excitations, including photoinduced electron transfer (PET) [10–14,16], formation of complexes with charge transfer [22], non-radiative transfer of electron excitation energy between the interaction components [15–17], intramolecular charge transfer [17], as well as internal filter effect [16–21]. However, achieving high concentration sensitivity and selectivity of the sensor is possible only under the condition of specific binding of the receptor and the analyte. Then, in addition to transformations caused by the photo-physical processes of [10–22], tetracycline molecules, due to the presence of amide and hydroxyl groups, can easily form chemical bonds (covalent and hydrogen type) with the QD interface, modifying it, which will also significantly affect the luminescent properties of QDs [23–32].

The structure of the quantum dots interface, determined by the nanocrystal environment, in particular the passivating ligand [26–32] and its modification by functionalization with transition metal ions, is specific for binding of the antibiotic and QDs, thus, providing luminescent response [24,25]. In paper [26], the impact of ligand on the sensory ability to detect tetracycline by ZnS QDs passivated by thiocarboxylic acids was analyzed, and it was shown that, depending on the type of ligand (3-mercaptopropionic acid (MPA) or 3-mercapto-1-propanesulfonic acid) the luminescence quenching efficiency, and, accordingly, the sensitivity limit of the receptor varies significantly.

The functionalization of QD interface by metal ions capable of forming coordination compounds with antibiotic molecules differs significantly from the case of doping a nanocrystal with metal ions. Thus, in paper jcite24, for the case of CdTe QDs interface functionalization (passivated with mercaptopropionic acid and glowing in the region of 698 nm) with Eu^{3+} ions (luminescent in the region of 617 nm),it was described that the addition of oxytetracycline does not affect QDs' luminescent properties in any way, by coordinating only with metal ions and changing the luminescence intensity of the latter. And in case of CdTe QDs doping with Cu ions, due to a change in the energy structure involving Cu *d*-orbital, the coordination of the antibiotic with metal has a significant effect (quenching) on the impurity luminescence band of QDs [23].

Therefore, for practical application of colloidal QDs as an antibiotic molecule sensor receptor it is relevant to

solve fundamental questions about the nature of antibiotic molecules interaction with QDs and its manifestation pattern in the spectral-luminescent properties in each specific case.

The issue of this kind of influence is particularly specific for QDs of silver chalcogenides with non-stoichiometric chemical composition. Such objects are characterized by the predominant role of the interface in the formation of spectral properties [32–43]. In particular, the nature of the luminescent band and its position depend on the state of the surface and environment of the nanocrystal [32–35]. In studies [32–43] it was shown that the passivating ligand and the wide-band semiconductor shell have great impact on the luminescent parameters of Ag_2S and Ag_2Se quantum dots. It is itself a new approach if we consider the use of recombination luminescence of Ag_2S QDs, the parameters of which depend on the state of the interface determined by both, the nanocrystal surface and the environment, as a highly sensitive luminescent sensor of tetracycline antibiotics. A detailed study of the effect of antibiotics presence in Ag_2S QDs solution on their luminescent properties will allow evaluating the potential for fabricating the sensors based on these samples to determine the presence of tetracycline antibiotics. The data obtained will have a very significant scientific value for the development of research and technical field of luminescent sensors.

This paper outlines experimental data demonstrating the effect that the molecules of oxytetracycline (OTC) antibiotic have on the luminescent properties of Ag_2S QDs with an average size of 2.8 nm passivated with thioglycolic acid molecules (Ag_2S/TGA QDs).

Materials and methods

Synthesis of colloidal Ag_2S/TGA QDs To obtain Ag_2S/TGA QDs in an aqueous solution, a two-component synthesis approach was implemented which included mixing of two precursors solutions and described in detail in papers [32–34]. As a first precursor a mix of water solutions of $AgNO_3$ ($3 \cdot 10^{-2}$ mol/L) and TGA ($1.5 \cdot 10^{-2}$ mol/L) was used with pH 10, aqueous solution of sodium sulfide Na_2S ($2.6 \cdot 10^{-2}$ mol/L) was used as a second precursor. The second solution was drip-injected into the first one under conditions of constant stirring and pH control of the medium. The resulting mixture was kept for a day at room temperature. To purify the colloid from the reaction products, it was dispersed in acetone, centrifuged, freed from liquid, and the resulting powder was dissolved in distilled water.

For the obtained samples, the structural properties were certified both, by transmission electron spectroscopy (TEM) and using well-known literature data for similar Ag_2S/TGA QDs synthesized according to this method [32–34].

TEM analysis made on Libra-120 showed for this method a synthesis of assemblies of individual Ag_2S/TGA quantum dots with an average size of 2.8 nm and dispersion of 7–25% (see Fig. 1, *a*). Detailed structural studies for such samples are presented in paper [32], where it was found that nanocrystals Ag_2S are formed in a monoclinic lattice (spatial group $P21/c$).

According to paper [33,34] in Ag_2S QDs passivation by TGA molecules is provided by the interaction of nanocrystal surface with sulfur atoms of the ligand. As a result, the QD interface has a structure as shown in Figure 1, *b*.

The mixes of Ag_2S/TGA QDs with the molecules of oxytetracycline (OTC) (Ag_2S/TGA QD-OTC) were prepared as described below. An ethanol solution of OTC was obtained at a concentration of 10^{-3} mol/L, which was then added to a colloidal QD solution in quantities that provided concentrations of the antibiotic in the solution of $4 \cdot 10^{-3}$, $9 \cdot 10^{-3}$, $1.3 \cdot 10^{-2}$, $1.8 \cdot 10^{-2}$, $2.2 \cdot 10^{-2}$ and $2.6 \cdot 10^{-2}$ mg/mL, which corresponds to the ratio ν(OTC): ν(KT Ag_2S/TGA) $= 0.6 \cdot 10^{-3}$, $1.3 \cdot 10^{-3}$, $2 \cdot 10^{-3}$, $2.6 \cdot 10^{-3}$, $3.3 \cdot 10^{-3}$. $4 \cdot 10^{-3}$ OTC mole/ QD mole (further, mole fraction or m.f.).

Research procedures The studies were carried out using luminescent and absorption techniques. The optical absorption spectra were studied using USB2000+ spectrometer (Ocean Optics, USA) with a USB-DT continuous radiation source (Ocean Optics, USA). The luminescence spectra of Ag_2S/TGA QDs were recorded using a spectral complex based on the MDR-4 diffraction monochromator (LOMO, Russia) with a near-IR photodetector PDF10C/M (ThorlabsInc., USA). Photoluminescence excitation was carried out by laser diodes 405MD-500-OX160 (China) with a wavelength of 405 nm and an optical power of 500 mW and GH0782RA2C (China) with a wavelength of 780 nm and optical power of 200 mW for Ag_2S/TGA QDs.

The kinetics of IR luminescence in the emission band of Ag_2S/TGA QDs was investigated using a PicoSingleTC-SPC system for time-correlated counting of photons with a InGaAsKIT-IF-25C single-photon detector (MicroPhotonDevices, Italy) and additionally using PMC-100-20 photomultiplier module with controller (Becker & Hickle) providing the system sensitivity in the region of up to 400–1400 nm. A PICOPOWERLD660 semiconductor pulse laser was used as an excitation source (with a wavelength of 660 nm, a pulse length of 60 ps) (Alphalas, Germany). Time resolution of this setup configuration was 0.12 ns and limited by characteristics of the single-photon detector.

Quantum yield of Ag_2S/TGA QDs luminescence was determined by the relative method using the following equation:

$$QY = QY_R \frac{I}{I_R} \frac{D_R}{D} \frac{n^2}{n_R^2}, \quad (1)$$

where QY_R — quantum yield of reference standard's luminescence, I and I_R — integral intensity in the sample and standard's luminescence band, D and D_R — optical density at the excitation wavelength for the sample and reference standard (in experiments it was ~ 0.1), n and

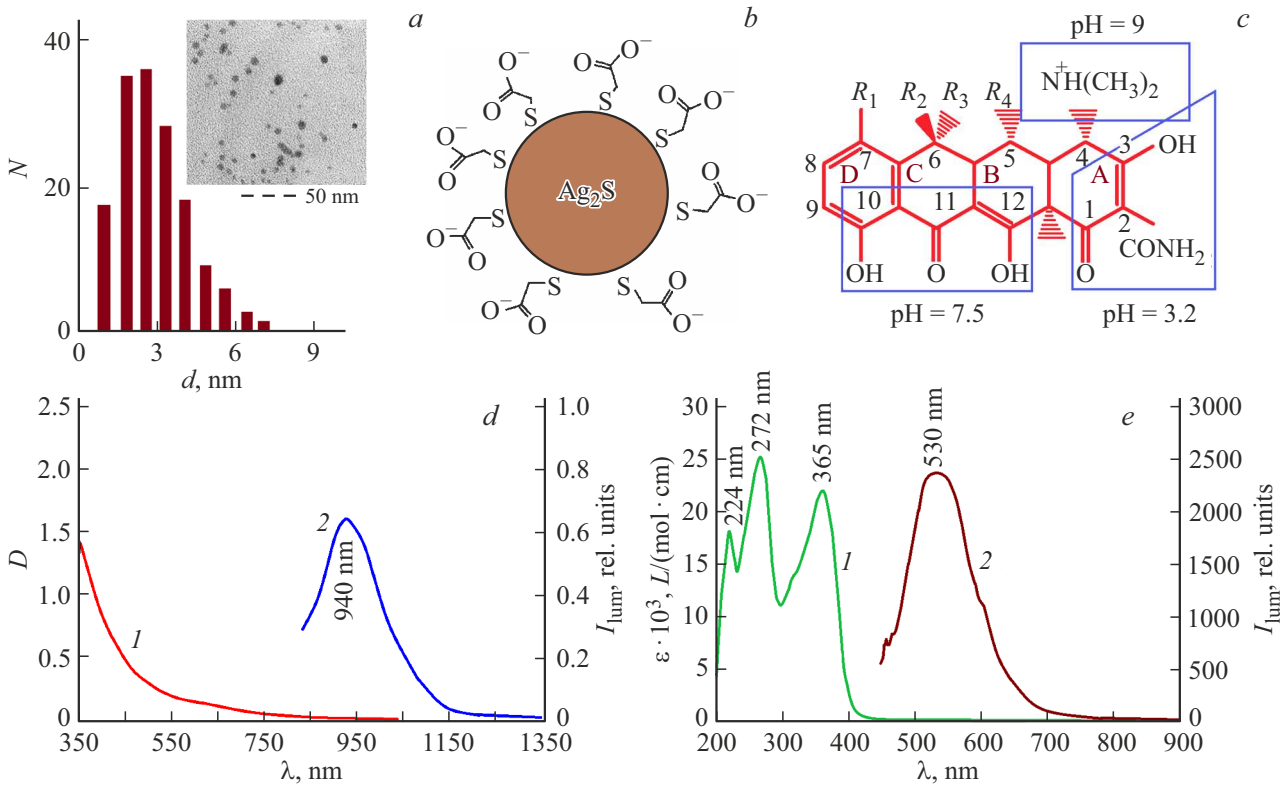

Figure 1. Structural and spectral properties of Ag_2S/TGA quantum dots and oxytetracycline: (*a*) PEM-image of assembly and size distribution (insert) of Ag_2S/TGA QDs, (*b*) diagram of Ag_2S QDs covered by the molecules of TGA ligand, (*c*) structural formula of oxytetracycline, (*d*) absorption spectrum (curve *1*) and luminescence spectrum (curve *2*) Ag_2S/TGA QDs, (*e*) absorption spectrum (*1*) and luminescence spectrum (*2*) of oxytetracycline.

n_R — refraction indices of solution with the sample and reference standard, respectively. An ethanol solution of ICG dye with a quantum yield of 14% in the region of 830 nm was used as the reference standard for the quantum yield of luminescence in IR region [44].

IR absorption spectra were recorded using FTIR-spectrometer Tensor 37 (Bruker Optik GmbH, Germany). For the study of IR spectra, colloidal QDs, as well as oxytetracycline solutions, were applied to KCl wafers and dried as quickly as possible to prevent severe degradation of the substrates. The deposited solutions had equal volumes and deposition temperatures.

Results and discussion

Spectral properties of components of Ag_2S/TGA QD-OTC mixture Let's consider spectral properties of individual components of Ag_2S/TGA QDs-OTC mixture. Optical absorption spectrum of Ag_2S/TGA QDs represents itself a wide band with a singularity in 780−810 nm region (Fig. 1, *d*),which corresponds to exciton ground state transitions for the studied QDs samples. Such „lack of structure" of Ag_2S/TGA QDs' absorption spectrum is associated with high non-stoichiometry of silver chalcogenides, as well as with dispersion of the nano-particles in the assembly [32,45].

The exact position of the main exciton transition was obtained from the analysis of $d^2D/d(h\nu)^2$ dependence, where D is the optical density of the colloidal QD solution, and $h\nu$ is the energy (in electron volts), and was about 1.55 eV, which corresponds to a wavelength of 800 nm. For the studied samples, the position of the main exciton transition exceeded the band gap for bulk Ag_2S with a monoclinic crystal structure by 0.55 eV (1.09 eV) [45].

In the luminescence spectra of the studied Ag_2S/TGA QDs, excited by both, the wavelength of 405 nm, and the wavelength of 780 nm, a luminescence band with a maximum of 940 nm and half-width of 0.2 eV was observed (Fig. 1, *d*). The significant half-width of the spectrum and the large Stokes shift (0.23 eV) relative to the main exciton transition allow us to conclude that the observed band is due to a recombination mechanism, namely, the recombination of a free hole with an electron localized at the impurity level — luminescence center [32].

In optical absorption spectra of OTC the two maxima at 272 and 365 nm are observed characteristic to the tetracycline molecules that correspond to $\pi \rightarrow \pi^*$-transitions in C=C (Fig. 1, PicoSingleTCSPC*e*). In literature these maxima are generally discussed as a contribution of two individual chromophores (a shorter wavelength peak (272 nm) corresponds to A ring and the longer wavelength peak

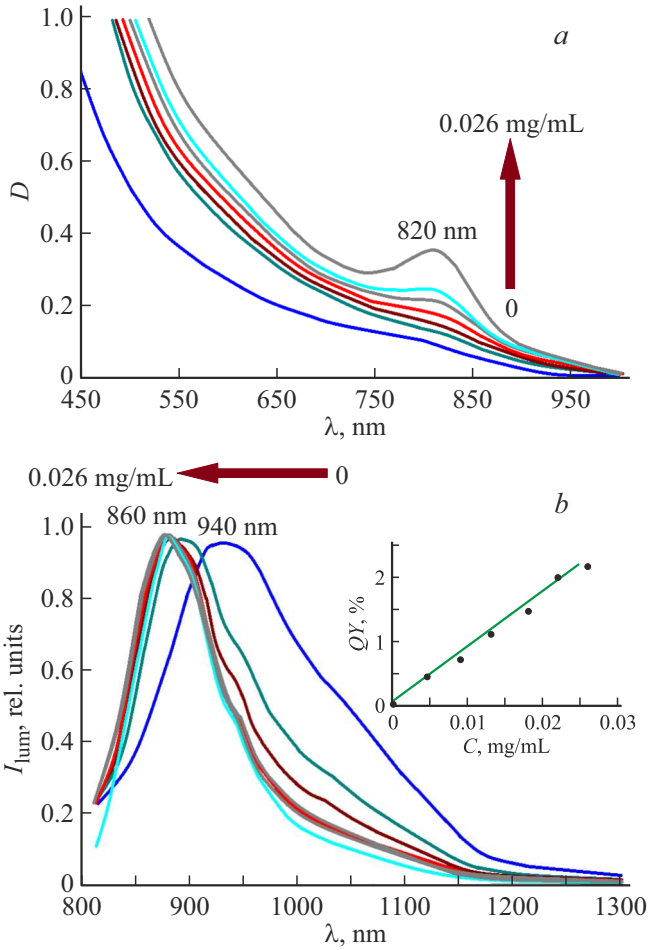

Figure 2. Spectra of optical absorption (a) and luminescence (b) of Ag_2S/TGA QDs in presence of oxytetracycline. Insert window to Figure (b) — Ag_2S/TGA QDs' QY luminescence versus antibiotic molecules concentration.

(365 nm) corresponds to BCD ring), Fig. 1, a, insert window [46,47]. The molar extinction coefficient of tetracycline in a solution is about 25000 L/(mol·cm) in the band with a maximum of 272 nm and 25000 L/(mol·cm) — 365 nm.

In OTC luminescence spectrum a wide band (FWHM = 0.5 eV) with a peak in 530 nm region is observed. The Stokes shift is about 1.1 eV (Fig. 1, e). The significant Stokes shift and half-width of the spectrum for an organic molecule are explained by the special nature of its luminescence associated with the presence of a short-lived „hot" singlet state S_1^*, which stabilizes over times of the order of 0.17–2.1,ps by oscillatory cooling to a relaxed medium-lived state S_1, from which the illumination occurs, as well as the presence of molecule tautomeric forms in the solvent [47,48].

Spectral properties of Ag_2S/TGA QD-OTC mixture

The absorption and luminescence spectra of Ag_2S/TGA QDs and OTC mixtures were analyzed at different concentrations of tetracycline molecules in solutions when excited by radiation with wavelengths of 405 and 780 nm. The first wavelength corresponds to both, the impurity absorption of Ag_2S/TGA QDs, and OTC absorption region. The introduction of oxytetracycline into the solution leads to significant changes in the absorption and luminescence spectra of colloidal Ag_2S/TGA QDs (Fig. 2). Thus, in the absorption spectrum, against the background of the structureless band of the initial Ag_2S/TGA QD sample, a singularity appears in the region 820–840 nm, which transforms into a band with a maximum of 820 nm for the maximum of the used concentrations of (ν(OTC) antibiotic: ν(KT Ag_2S/TGA) = $4 \cdot 10^{-3}$ m.f.).

In the luminescence spectrum of Ag_2S/TGA QDs in a mixture with OTC, a shift of the maximum radiation to the short-wavelength region is observed as the antibiotic concentration in the solution increases reaching a limiting value of 860 nm (Fig. 2, b). The quantum yield of luminescence increases linearly with increasing concentration of OTC in the mixture. The values QY for different combinations are presented in Table below. We see that at maximal concentration among the used concentrations (ν(OTC): ν(QD Ag_2S/TGA) = $4 \cdot 10^{-3}$ m.f.) QY grew by two orders and made 2.18%.

It can be seen that the luminescence band when adding OTC to the DC solution is not elementary and can be represented by two bands with maxima of 860 and 940 nm (Fig. 3, a).

Parameters of luminescent curves were analyzed for these bands (Fig. 3, a, Table). As may be seen the half-width of the bands doesn't differ much and makes 0.13 and 0.16 eV for bands with peaks of 860 and 940 nm, respectively. However, the Stokes shift relative to the peak in absorption (820 nm) has a threefold decrease. Additionally, the luminescence attenuation curves in the corresponding bands 860 and 940 nm were investigated (Fig. 3, b).

The average luminescence decay time $\langle\tau\rangle$ for Ag_2S/TGA QDs and their mixtures with OTC molecules were obtained from experimental luminescence decay curves $I(t)$ using the approximation expressions

$$I(t) = \sum_{i=1}^{2} \alpha_i \exp\left(-\frac{t}{\tau_i}\right),$$

$$\langle\tau\rangle = \frac{\sum_{i=1}^{2} a_i \tau_i}{\sum_{i=1}^{2} a_i}, \qquad (2)$$

where a_i — amplitude, τ_i — time component constant with a number i.

The obtained values of the average luminescence decay time are shown in the table. For the quantum dots Ag_2S/TGA the luminescence decay time has the same order of magnitude for both bands and makes 3.4 and 3.7 ns for 860 and 940 nm respectively. The estimated values correspond to the values of the average decay time of trap-state luminescence of Ag_2S/TGA QDs outlined in

Luminescent characteristics of the studied samples

Sample	QD Ag_2S/TGA	ν(OTC): ν(QD Ag_2S/TGA) $= 0.6 \cdot 10^{-3}$ m.f.	ν(OTC): ν(QD Ag_2S/TGA) $= 1.3 \cdot 10^{-3}$ m.f.	ν(OTC): ν(QD Ag_2S/TGA) $= 2 \cdot 10^{-3}$ m.f.	ν(OTC): ν(QD Ag_2S/TGA) $= 2.6 \cdot 10^{-3}$ m.f.	ν(OTC): ν(QD Ag_2S/TGA) $= 3.3 \cdot 10^{-3}$ m.f.	ν(OTC): ν(QD Ag_2S/TGA) $= 4 \cdot 10^{-3}$ m.f.
λ_{lum}, nm	940	900	880	870	860	860	860
QY, %	0.04	0.54	0.73	1.12	1.47	2.10	2.18
τ_{860}, ns	3.7						6.6
τ_{940}, ns	3.4						4.8

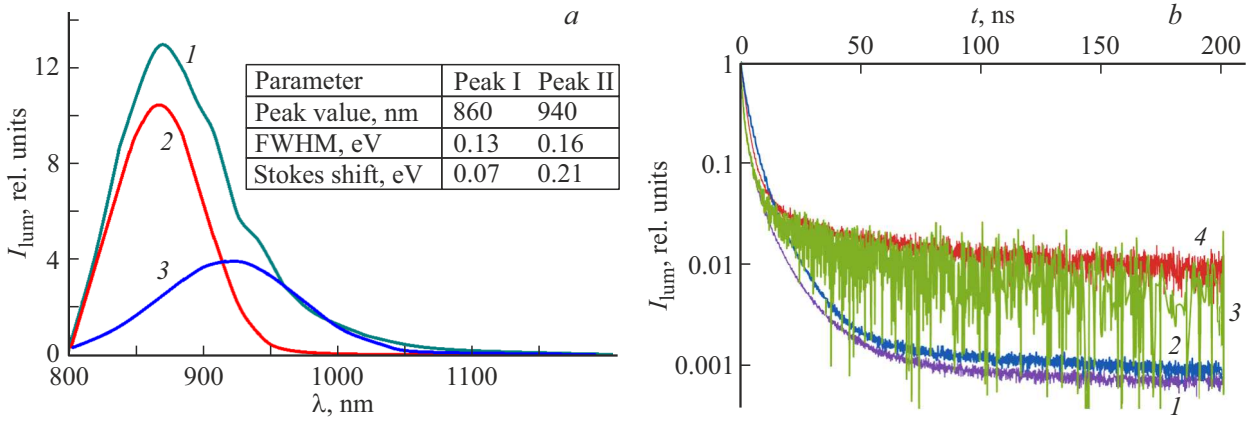

Figure 3. Decomposition of the luminescence band into two components (*a*): experimental spectrum (curve *1*), component *1* (curve *2*) and component 2 (curve *3*) and kinetics of the luminescence decay in the appropriate bands (*b*): Ag_2S/TGA QDs in 860 nm band (curve *1*), Ag_2S/TGA QDs + OTC in 860 nm band (curve *2*), Ag_2S/TGA QDs in 940 nm band (curve *3*), Ag_2S/TGA QDs,+ OTC in 940 nm band (curve *4*).

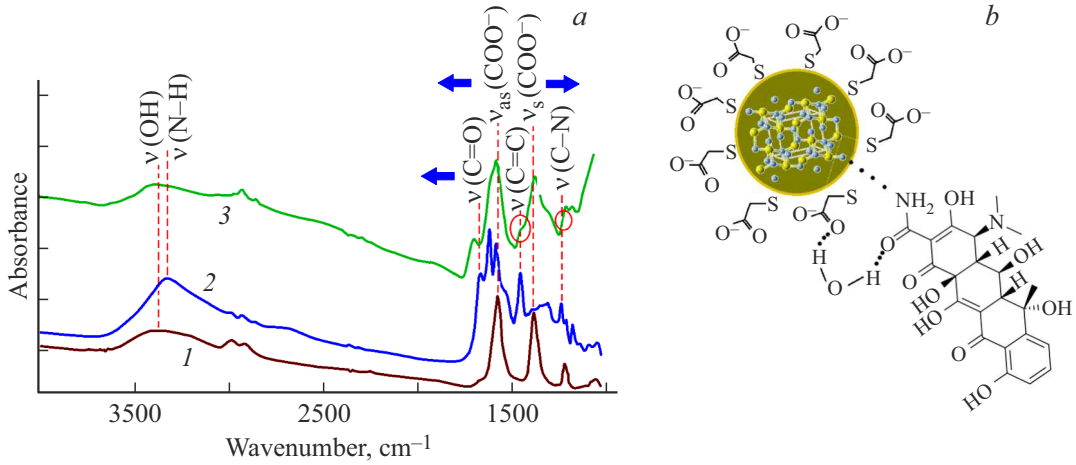

Figure 4. (*a*) IR absorption spectra of the studied samples: *1* — Ag_2S/TGA DCs, *2* — OTC (10^{-3} mol/L) in ethanol, *3* — Ag_2S/TGA QDs + OTC. (*b*) Diagram of OTC molecules interaction with Ag_2S/TGA QDs.

the literature [32–34]. At the same time, in the exciton luminescence band for Ag_2S/TGA QDs, the luminescence decay time is less than 1 ns [32]. Combined with FWHM values, the data on average decay times allow us to conclude about the recombination nature of the luminescence in both bands.

When OTC is added to the QD solution, the kinetics of luminescence decay slows down in both bands, and the luminescence decay times increase to 6.6 and 4.8 ns for 860 and 940 nm, respectively.

Obviously, the observed changes are related to the impact of OTC molecules on the absorption and luminescent properties of Ag_2S/TGA QDs. First of all, we note that this effect is not related to the processes of reabsorption and exchange of electronic excitations, since the nature of the observed regularities remains constant both for excitation of

405 nm and for excitation by radiation with a wavelength of 780 nm, which falls on the absorption region of only one of the components of the mixture (Ag_2S/TGA QDs). Apparently, the observed changes are related to a change in QDs interface structure in mixture with OTC molecules due to the interaction between the components.

To identify the interaction mechanisms the IR absorption spectra of mixtures of Ag_2S/TGA QDs and OTC molecules were examined (Fig. 4, *a*). When the antibiotic is added to Ag_2S/TGA QDs sufficient changes are observed in the IR absorption spectra (Fig. 4, *a*). In the high-frequency domain a wide peak was observed in $3370-3320\,cm^{-1}$ region which is explained by a sum of stretch vibrations signals of the bound OH- and NH_2-groups [33,34,49]. The singularity in the region corresponding to the deformation vibrations of the amide band ($1520-1500\,cm^{-1}$) also disappears [49]. Such singularities, when the QDs are mixed with OTC, together with the hypsochromic shift of the stretch vibrations band C=O (Amide I) (from $1665\,cm^{-1}$ to $1680\,cm^{-1}$) [49] indicate that there's an interaction between the tricarbonyl system of the antibiotic (C1–C3 in Fig. 1, *c*) with the quantum dots Ag_2S/TGA. At that, the shift of stretch vibrations of the group COO- ($1573\,cm^{-1}$ to $1582\,cm^{-1}$, $1383\,cm^{-1}$ to $1397\,cm^{-1}$) for TGA molecules indicates their participation in the hydrogen bonds with carbonyl in the presence of water molecules. Schematic representation of such interaction is illustrated in Fig. 4, *b*, insert window.

Thus, the analysis of IR spectroscopy data shows that OCT molecules „additionally passivate" the surface of Ag_2S/TGA QDs due to the interaction of the tricarbonyl group with dangling bonds of QDs interface and molecules of passivating ligand (TGA), providing luminescence flare of the QDs. In this case, the recombination nature of luminescence in the 860 nm band is explained by the relatively small Stokes shift of the luminescence band relative to the absorption peak (820 nm) due to the formation of new luminescence centers close in energy to the bottom of the conduction band. The study of the structural and energy parameters of these centers is to be reviewed in a separate paper.

It should be emphasized that the obtained findings show that there's a potential for practical application of colloidal solution of Ag_2S/TGA QDs as a luminescent sensor to detect the presence of oxytetracycline in the solution which is evidenced by enhancement of the luminescent signal with the increase in concentration of antibiotic molecules.

Conclusion

In this study the impact of oxytetracycline on the absorption and luminescent properties of Ag_2S/TGA QDs was investigated. In the presence of oxytetracycline molecules, a transformation of the spectral properties of Ag_2S/TGA QDs is observed: a peak appears in the region of 820 nm, which is caused by the absorption of the basic exciton state of QDs, while in the luminescence spectrum there is a 10-fold increase in luminescence intensity and a shift of the band maximum to the short-wavelength region. It is demonstrated that the observed spectral patterns are explained by „additional passivation" of Ag_2S/TGA QDs' surface due to the coupling of dangling bonds of QDs interface and TGA molecule with the tricarbonyl system of OTC. Such „additional passivation" can lead to the formation of additional radiative recombination channels with the participation of luminescence centers formed in the presence of antibiotic molecules and close to the bottom of QD conduction band in terms of energy.

Acknowledgments

The author expresses his thanks to O.V. Ovchnnikov, Dr. Sci. in Physics and Mathematics, and M.S. Smironov, Dr. Sci. in Physics and Mathematics, for their participation in the discussion of the findings.

Funding

This study was supported by the Russian Science Foundation (project №. 24-29-00668).

Conflict of interest

The authors declare no conflict of interest.

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Translated by T.Zorina