



Original articles

Research article

<https://doi.org/10.17308/kcmf.2023.25/11258>**Formation of plasmon-exciton nanostructures based on quantum dots and metal nanoparticles with a nonlinear optical response**

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1 Universitetskaya pl., Voronezh 394018, Russian Federation**Abstract**

The establishment of the conditions for the formation of nanostructures with plasmon-exciton interaction based on quantum dots and plasmonic nanoparticles that provide unique nonlinear optical properties is an urgent task. The study demonstrates the formation of plasmon-exciton nanostructures based on hydrophilic colloidal $Zn_{0.5}Cd_{0.5}S$, Ag_2S quantum dots and metal nanoparticles.

Transmission electron microscopy and optical absorption and luminescence spectroscopy were used to substantiate the formation of plasmon-exciton hybrid nanostructures. The phase composition of the studied samples was determined by X-ray diffraction. The results obtained using ARLX'TRA diffractometer (Switzerland) indicated a cubic crystal structure ($F\bar{4}3m$) of synthesised $Zn_{0.5}Cd_{0.5}S$ quantum dots and monoclinic ($P2_1/C$) crystal lattice of Ag_2S . Transmission electron microscopy revealed that plasmonic nanoparticles are adsorption centres for quantum dots. The average sizes of the studied samples were determined: colloidal Ag_2S quantum dots (2.6 nm), $Zn_{0.5}Cd_{0.5}S$ (2.0 nm) and metal nanoparticles: silver nanospheres (10 nm) and gold nanorods (4x25 nm). The transformation of the extinction spectra of the light and the luminescence quenching of quantum dots have been established in mixtures of quantum dots and plasmonic nanoparticles. The nonlinear optical parameters of the studied samples were determined using the Z-scanning method at wavelengths of 355 and 532 nm in the field of nanosecond laser pulses. The conditions for the formation of hybrid nanostructures that provide an increase of the coefficient of nonlinear absorption of laser pulses (355 and 532 nm) up to 9 times with a duration of 10 ns due to the reverse saturable absorption occurring due to cascade two-quantum transitions in the intrinsic and local states of colloidal quantum dots and the suppression of nonlinear refraction, were determined.

The observed changes were explained by the manifestation of the Purcell effect on the states of quantum dots in the presence of nanoresonators (gold nanorods and silver nanospheres). The results of these studies create new opportunities for the development of original systems for controlling the intensity of laser radiation, as well as quantum sensors of a new generation.

Keywords: Nonlinear refraction, Nonlinear absorption, Quantum dot, Ag_2S , $Zn_{0.5}Cd_{0.5}S$, Plasmonic nanoparticle, Z-scan

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1. Introduction

The creation of hybrid nanostructures with a “plasmon-exciton” interaction based on plasmonic nanoparticles (NPs) of noble metals, semiconductor quantum dots (QDs), and/or dye molecules recently became a promising and urgent task [1]. The properties of such nanostructures, which are not characteristic of individual components, primarily optical ones, and the problem of their prediction and control is especially topical and of interest. They are determined both by the composition and spectral resonances of the components and by the mechanisms of intermolecular interactions. The interaction between the components of such hybrid systems is manifested in the absorption and luminescence spectra of QDs and the extinction spectra of nanoparticles. In the case of luminescence, the manifestation of the interaction of components is often the signs of the exchange of electronic excitations between the components of the nanosystem [2–4], as well as the effects of plexiton coupling that occurs upon electronic excitation of the system [1, 5–7]. In the latter case, the tuning of the optical resonances of the structure components, e.g., the degree of their overlap, is of fundamental importance.

A separate problem in the physics of plasmon-exciton nanostructures is the establishment of the conditions for their formation, which provide a significant modification of the nonlinear optical properties of their components. Similar systems can be used for quantum sensorics. In a number of studies, the possibility of modifying/hybridising the nonlinear optical properties of dye molecules adsorbed on plasmonic nanoparticles was discovered [4, 8, 9]. In such hybrid nanostructures, the processes of transfer of electronic excitations provide changes in the nonlinear optical response. The interaction in mixtures of spherical gold nanoparticles and methylene blue dye enhances the reverse saturable absorption due to the Purcell effect, which manifests as an increase in the probability of triplet-triplet absorption of methylene blue [10]. The conditions for the formation of nanostructures with a plasmon-exciton interaction based on quantum dots and plasmonic nanoparticles, which provide unique nonlinear optical properties, still remain unclear.

This study partially fills this gap and is devoted to establishing the laws governing the formation of plasmon-exciton nanostructures based on colloidal Ag_2S (2.6 nm), $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ (2.0 nm) quantum dots, passivated with thioglycolic acid, and silver and gold nanoparticles, providing an 8–9-fold increase in nonlinear absorption in QDs.

2. Experimental

The studied samples were synthesised using the aqueous colloidal synthesis methods. In the synthesis of colloidal Ag_2S QDs, passivated with thioglycolic acid (TGA), the silver precursor was an aqueous solution of silver nitrate (AgNO_3). An aqueous solution of TGA was added to this solution with constant stirring, and the Ag-TGA complex was formed. As the pH of the solution increased to 11, the solution became clear. Next, an aqueous solution of Na_2S was added as a source of sulphur. Molar ratios of TGA/ AgNO_3 / Na_2S precursor were 2:1:0.5. $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs were synthesised in a similar way, except that the pH of the Zn(Cd)-TGA complex was increased to 7. For the removal of the reaction products after synthesis, QDs were precipitated by centrifugation with the addition of ethanol and redispersed in water.

Gold nanorods (Au NRs) were formed using multistage colloidal synthesis [11]. An aqueous solution of the surfactant cetyltrimethylammonium bromide (CTAB) was used for the growth of cylindrical NRs, being both a weak reducing agent and an anisotropic medium. Initially, a seed solution of gold nanospheres 3 nm in size was obtained by reducing aqueous chloroauric acid HAuCl_4 (7 μl , 0.36 mol) by NaBH_4 solution (1.0 ml, 5 mmol) in CTAB aqueous solution (20 ml, 0.02 mmol). The growth anisotropy of NPs was ensured by introducing a mixture of HAuCl_4 (28 μl , 0.36 mol), CTAB (50 ml, 0.1 mmol), AgNO_3 (0.1 ml, 0.02 mol) and $\text{C}_6\text{H}_8\text{O}_6$ (5 ml, 0.05 μmol). The addition of AgNO_3 contributes to the control of the length-to-diameter ratio of Au NRs.

The synthesis of silver nanoparticles of spherical geometry (Ag NP) is based on the successive reduction of silver nitrate AgNO_3 by sodium borohydride (NaBH_4) and stabilisation with sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and hydrogen peroxide (H_2O_2). Potassium bromide (KBr) limits

the growth of silver nanoparticles, which leads to the production of nanospheres of a given size [12]. The prepared colloidal solutions of metal nanoparticles were purified from reaction products by washing with distilled water through several centrifugation–dispersion cycles. Mixtures of the studied samples were prepared by introducing a solution of metal nanoparticles into a QDs solution.

The size of the studied QDs and metal nanoparticles was determined using a Libra 120 transmission electron microscope (TEM) (Carl Zeiss, Germany) with an accelerating voltage of 120 kV. The phase composition of the studied samples was determined by X-ray diffraction; the results were obtained on an ARLX'TRA diffractometer (Switzerland) with the $K\alpha_1$ radiation of a copper line (1.54056 Å). Optical absorption and luminescence spectra were recorded using USB2000+ spectrometer (OceanOptics, USA) with a USB-DT radiation source (OceanOptics, USA). The luminescence decay kinetics of QDs was measured using a TimeHarp-260 module (PicoQuant, Germany) operating in the single photon counting mode. The detector was a PMT PMC-100-20 (Becker&Hickl Germany) with a time resolution of 0.2 ns. The luminescence decay curves were approximated by the theoretical curve using the deconvolution procedure with the experimentally measured instrument response function.

Analysis of the nonlinear optical response of the studied samples was performed using the

Z-scan method [13]. This method is based on measuring the normalised transmission of the test sample as it moves relative to the focal plane of a converging lens along the optical z axis. The normalised transmittance was determined as the ratio of the sample transmittance $T(z)$ at the point with coordinate z to the sample transmittance in the linear mode at low intensity, which is recorded far from the lens focus $T(z \rightarrow \infty)$. In this method, the transmission of the sample was measured under the condition of different transverse dimensions of the Gaussian beam (different intensities). In other words, when changing the z coordinate, the scanning according to the laser radiation intensity was actually carried out.

We used the radiation of the third and second harmonics of YAG:Nd³⁺ laser (LS-2132UTF, LOTIS TII) with a wavelength of 355 and 532 nm, respectively, a duration of 10 ns and a repetition rate of 1 Hz. The radiation was focused by a spherical lens with a focal length of 300 mm. Quartz cuvettes with the thickness of 5 mm containing the studied samples were moved along the optical z axis of the probing laser pulse through the focal plane of the collecting lens using a linear translator. The waist radius was ~30 μm. The measurements were carried out using pulse energies of 1.33 mJ (355 nm) and 0.16 mJ (532 nm).

3. Results and discussion

TEM images of the initial components and their mixtures are shown in Fig. 1. It can be seen

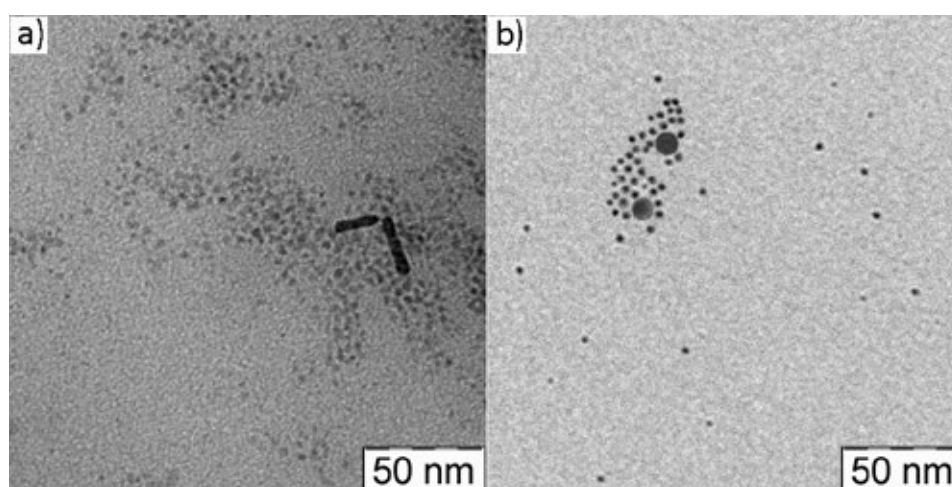


Fig. 1. TEM images of synthesised Ag₂S QDs conjugated with gold nanorods (a), Zn_{0.5}Cd_{0.5}S QDs conjugated with silver nanospheres (b)

from Fig. 1a. individual QDs of Ag_2S with an average size of 2.6 nm with a size dispersion of 20–30% were formed within the framework of the used approaches to synthesis. The resulting gold nanoparticles were nanorods with an average size of 4×25 nm (Fig. 1a). According to TEM images, $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs had an average ensemble size of 2.0 nm at the same dispersion (Fig. 1b). Silver nanoparticles Ag NPs of spherical geometry had an average size of 10 nm. According to X-ray diffraction data, it was possible to establish a cubic crystal structure ($F\bar{4}3m$) for $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs (Fig. 2a). The diffraction pattern of Ag_2S QDs was a system of broadened reflections against the background of a noticeable halo, corresponding to the monoclinic ($P2_1/C$) Ag_2S crystal lattice (Fig. 2a). Figure 2b shows X-ray diffraction patterns of Ag and Au nanoparticles.

The diffraction peaks at 38, 44, 64, and 77° corresponded to the (111), (200), (220), and (311) planes of the face-centred cubic crystal lattice. It has been found that plasmonic nanoparticles are adsorption centres for quantum dots. The TEM images showed the largest accumulation of QDs near Au NRs and Ag NPs (Fig. 1). Thus, it has been established that the approaches used for the synthesis of mixtures of QDs of metal nanoparticles ensure the compatibility of the components in the formation of hybrid structures.

Optical absorption spectra of colloidal solutions of Ag_2S QDs were broad bands with an exciton peak at 810 nm (1.53 eV) (Fig. 3a, black curve), which was due to the quantum size effect, since the band gap of bulk Ag_2S crystals is 1.0 eV. Luminescence spectrum of Ag_2S QDs was a broad band with a peak at 881 nm (Fig. 3b, black curve).

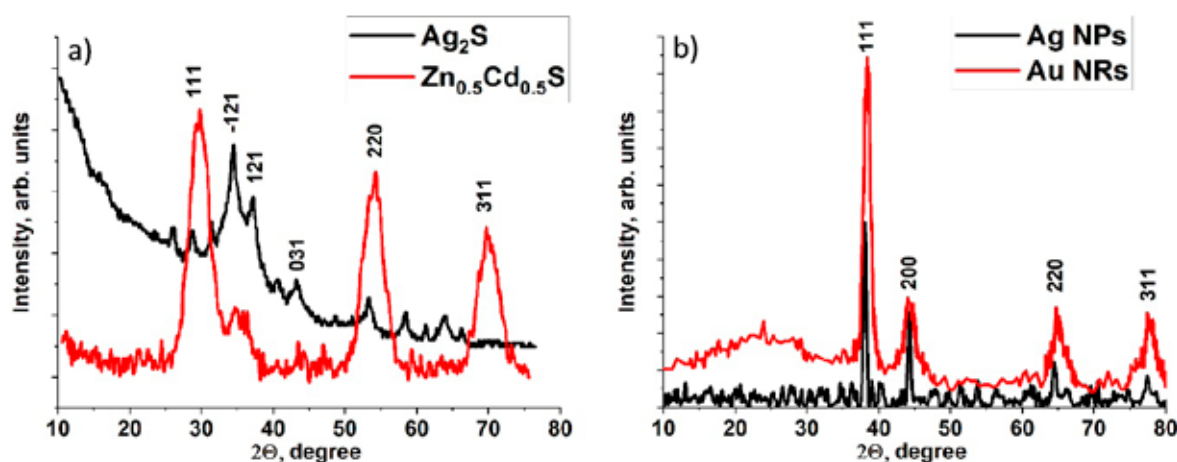


Fig. 2. X-ray diffraction obtained on Ag_2S and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs (a) and silver and gold nanoparticles

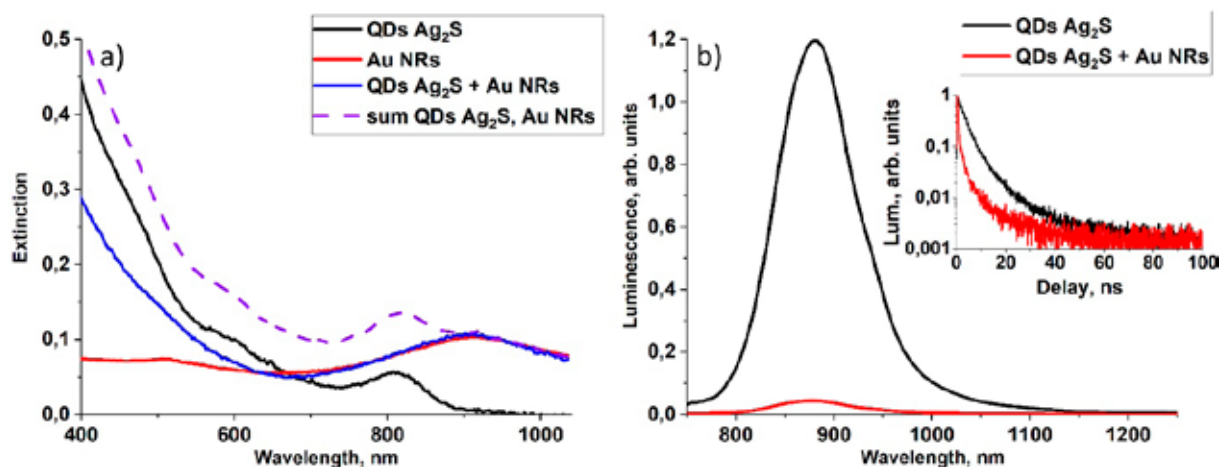


Fig. 3. Light extinction spectra of synthesised Ag_2S QDs, Au NRs and their mixtures (a) and luminescence spectra of Ag_2S QDs and their mixtures with Au NRs (b). The inset shows the luminescence decay kinetics of the studied samples

The light extinction spectrum of Au NRs consisted of two broad bands with peaks at 523 and 910 nm (Fig. 3a, red curve). The short-wavelength band is determined by the transverse plasmon resonance in Au NRs, while the long-wavelength band was determined by the longitudinal one [14]. Thus, the peak of the longitudinal plasmon resonance of Au NRs coincided with the luminescence band of Ag₂S QDs.

Such tuning of resonances in the extinction of light and luminescence of nanostructures suggests the possibility of the exchange of electronic excitations between the components of the nanosystem. In the extinction spectra of mixtures of Ag₂S QDs and Au NRs hybrid association was manifested as the disappearance of the feature associated with exciton absorption in Ag₂S QDs, and a decrease in the extinction of two components in the region of 400–600 nm (Fig. 3a, blue curve). The resulting extinction spectrum is not the sum of the extinction spectra of the components of the hybrid associate (Fig. 3a, purple curve), which indirectly indicated the manifestation of interaction in the resulting mixture [15–20]. Luminescence spectrum of Ag₂S QDs in the presence of gold nanorods demonstrates a decrease in the luminescence intensity by 27 times (Fig. 3b, red curve). It should be noted that this quenching cannot be explained by the filter effect alone. Approximation of the luminescence decay kinetics (Fig. 3b, inset) allowed to determine the luminescence decay time. Pure Ag₂S QDs showed an average

luminescence decay time of 5.2 ns, while for a mixture with gold nanorods it was 1.5 ns, i.e., 3.5 times lower. Luminescence quenching, accompanied by a reduction in the luminescence decay time, indicated a resonant nonradiative transfer of excitation energy from radiative recombination centres to plasmonic nanoparticles as a result of plasmon–exciton interaction. In this case, there were no characteristic features of the manifestation of the Purcell effect in Ag₂S QDs in the presence of Au NRs.

In the absorption spectrum of Zn_{0.5}Cd_{0.5}S QDs, a peculiarity in absorption associated with the most probable transition at a wavelength of 341 nm was observed. The extinction spectrum of Ag NPs had a plasmon resonance peak with a maximum at 400 nm (Fig. 4a). When pairing these nanostructures, an increase in the extinction of the mixture was observed in the wavelength range of 380–600 nm. Luminescence spectrum of Zn_{0.5}Cd_{0.5}S QDs was a broad band peaking at 480 nm. A significant Stokes shift of 1 eV relative to the exciton absorption peak indicates the recombination nature of the luminescence. When the data for QDs were paired with Ag NPs, luminescence quenching by 2 times was observed (Fig. 4b) and the luminescence kinetics accelerated from 446 to 348 ns. Quenching of the luminescence, acceleration of the kinetics, and change in the extinction of the obtained nanostructure indicated a resonant nonradiative transfer of the excitation energy from the QDs to the plasmonic nanoparticle.

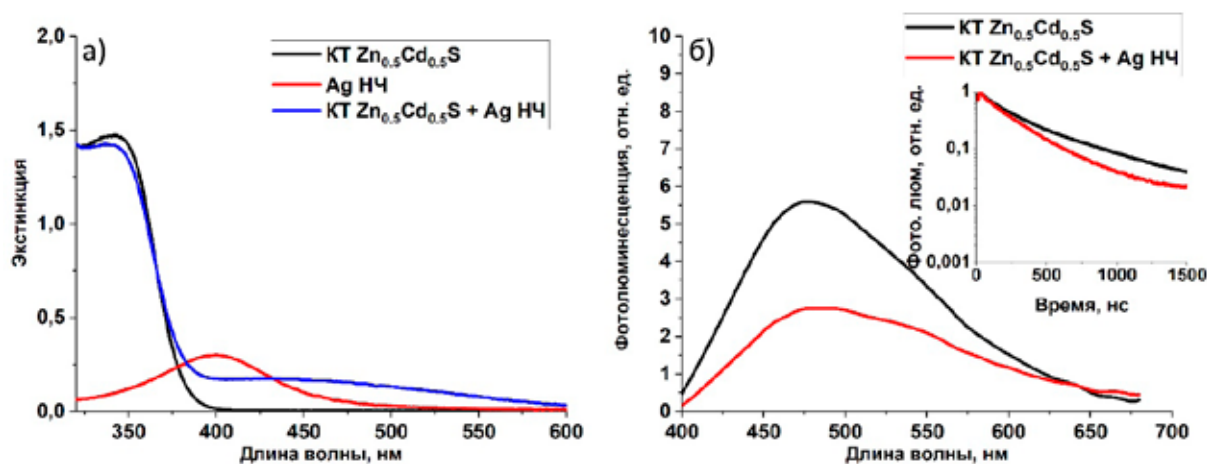


Fig. 4. Extinction spectra of synthesised Zn_{0.5}Cd_{0.5}S QDs, Ag NPs, and their mixtures (a) and luminescence spectra of Zn_{0.5}Cd_{0.5}S QDs, Ag NPs (b). The inset shows the luminescence decay kinetics of the studied samples

We will consider the nonlinear optical properties of the studied samples. The obtained Z-scans of the initial components and the hybrid nanostructure based on Ag_2S QDs, Au NRs are shown in Fig. 5a. There was a noticeable increase in the nonlinear absorption upon association of Ag_2S QDs, Au NRs compared to the original QDs (dip in the focal plane of the converging lens at $z = 0$). A colloidal solution of pure Au NRs did not show a nonlinear optical response under our experimental conditions (Fig. 5a, blue straight line). Z-scan of Ag_2S QDs obtained in closed-aperture geometry demonstrate defocusing of laser radiation, which is suppressed upon association with gold nanorods.

In the case of probing with laser pulses with a wavelength of 355 nm, $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs, Ag NPs, a picture similar to the previous result was observed. Significant increase in nonlinear absorption was observed, when $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs and Ag NPs were coupled. This pattern was not a manifestation of the sum of effects in the nonlinear optical response, since no useful signal was found in the study of metal nanoparticles, and quantum dots had a significantly lower nonlinear absorption (a dip in the focal plane in the Z-scan).

For further consideration of the above picture, it is worth referring to the nonlinearity mechanisms in the studied structures. For Ag_2S and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ quantum dots are characterised by

the nonlinear refraction of laser radiation. The defocusing of laser radiation arises due to the band filling effect [21, 22]. The filling of localised states is redistributed under the action of laser pulses on colloidal QDs, which in turn will lead to a change in the refractive index of the colloidal solution in accordance with the Kramers–Kronig relations [13]. The mechanism of nonlinear absorption in this case is the reverse saturable absorption on real states, which are traps (broken bonds on the QDs surface and structural defects) and/or luminescence centres. This was confirmed by the results of our studies [23–25]. Noble metal nanoparticles are characterised by bleaching of plasmon resonances in the field of femtosecond pulses, dynamic scattering, and photodestruction in the field of picosecond and nanosecond pulses [26]. In our experiments, the contribution of the dynamic scattering into the nonlinear optical response is low, as was experimentally confirmed by recording the signal on an additional photodiode located at an angle to the optical axis of the converging lens during Z-scanning. The absence of dynamic scattering was determined by the weak extinction of Au NRs solutions at the probing wavelength and the low energy of laser pulses.

Thus, an increase in nonlinear absorption was observed upon conjugation of QDs and plasmonic nanoparticles. The experimentally obtained Z-scans were approximated by the expression

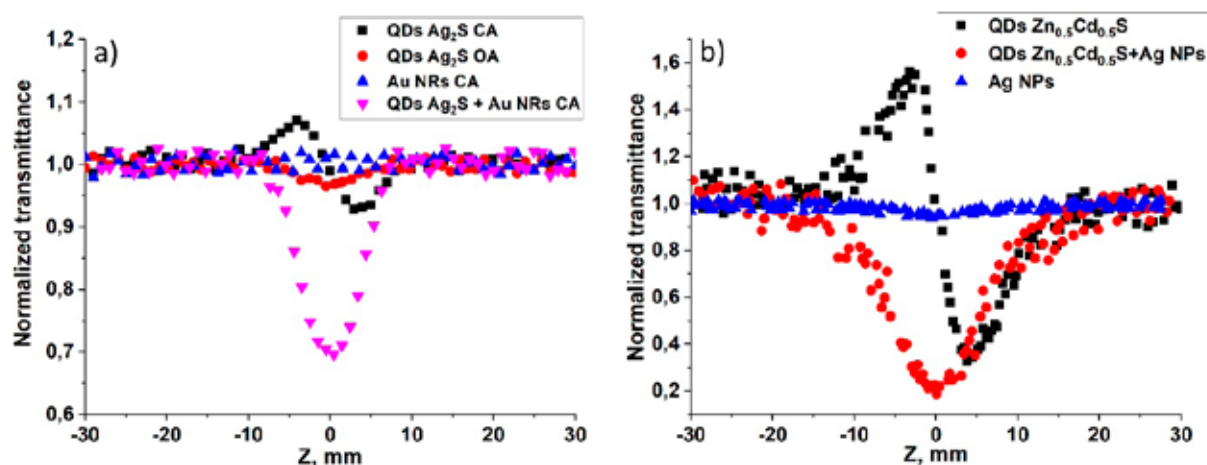


Fig. 5. Z-scan curves of the investigated Ag_2S QDs samples, Au NRs and their mixtures in the field of laser pulses with a wavelength of 532 nm, a duration of 10 ns and a pulse energy of 0.16 mJ, obtained in open (OA) and closed (CA) aperture geometry (a). Z-scan curves of the investigated $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs, Ag NPs samples and their mixtures in the field of laser pulses with a wavelength of 355 nm, a duration of 10 ns, and pulse energy of 1.33 mJ obtained in a geometry with a closed aperture

given in [27], which allowed to determine the coefficients of nonlinear absorption and nonlinear refraction. Nonlinear refraction coefficient of Ag_2S QDs was $-2.5 \cdot 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, non-linear absorption coefficient $-8 \cdot 10^{-11} \text{ cm} \cdot \text{W}^{-1}$. Nonlinear absorption coefficient of Ag_2S QDs and Au NRs mixture and was $7 \cdot 10^{-10} \text{ cm} \cdot \text{W}^{-1}$, which was 8.5 times higher than that of pure Ag_2S QDs. In the case of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs non-linear refraction coefficient was $-1 \cdot 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, nonlinear absorption coefficient was $1.4 \cdot 10^{-11} \text{ cm} \cdot \text{W}^{-1}$. Conjugation with silver nanospheres led to an increase in the nonlinear absorption coefficient up to $1.3 \cdot 10^{-10} \text{ cm} \cdot \text{W}^{-1}$, i.e., by 9.3 times compared to pure $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs. This increase in nonlinear absorption can be explained by an increase in reverse saturable absorption occurring as a result of cascade two-quantum transitions in the intrinsic and local states of colloidal quantum dots in the presence of plasmonic metal nanoparticles due to resonant non-radiative energy transfer resulted from plasmon-exciton interaction.

4. Conclusion

Substantiation of the formation of nanostructures with plasmon-exciton interaction based on $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$, Ag_2S quantum dots and silver and gold nanoparticles of spherical and cylindrical shape, respectively was performed using transmission electron microscopy and absorption and luminescence spectroscopy. The studied samples were selected taking into account different settings of optical resonances in absorption, luminescence of QDs, and extinction of metal nanoparticles. Experimental confirmation of the formation of hybrid plasmon-exciton nanostructures was the analysis of TEM images showing the adsorption of QDs on metal nanoparticles, as well as the transformation of the light extinction spectra of the mixture of QDs and NPs. The quenching of the QDs luminescence and the acceleration of its kinetics also indicated an interaction sufficient for resonant non radiative transfer of the electronic excitation energy from the recombination luminescence centres of QDs to plasmonic nanoparticles. For Ag_2S QDs and cylindrical gold nanoparticles mixture and $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ QDs with silver nanoparticles mixture in the pulsed laser field with a wavelength of 355 nm, an increase in the nonlinear absorption

coefficient of QDs in the presence of plasmonic metal nanoparticles up to 9 times was established using Z-scan method in the field of nanosecond laser pulses with a wavelength of 532 nm. The results of these studies create new opportunities for the development of original systems for controlling the intensity of laser radiation, as well as quantum sensors of a new generation.

Author contributions

A. I. Zvyagin – conducting scientific research, writing of the article, scientific editing of the text. T. A. Chevychelova – conducting scientific research. A. S. Perepelitsa – conducting scientific research. M. S. Smirnov – scientific editing of the text, discussion of the results of the study. O. V. Ovchinnikov – scientific editing of the text, discussion of the results of the study.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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