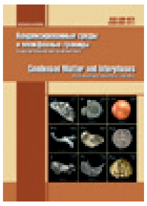

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Formation of hybrid nanostructures based on $Zn_{0.5}Cd_{0.5}S$ quantum dots and silver nanoparticles for nonlinear optical applications in the near ultraviolet

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Abstract

The goal of this study was to establish optimal conditions for the formation of hybrid nanostructures based on quantum dots and metal nanoparticles with a nonlinear optical response in the near ultraviolet. The relevance of this study is confirmed by the need to create passive devices for controlling the parameters of laser radiation in the presence of semiconductor colloidal quantum dots (QDs) and plasmonic nanoparticles (NPs). Manifestations of interaction in the nonlinear optical response of $Zn_{0.5}Cd_{0.5}S$ QDs and spherical Ag NPs (10 nm) in the field of laser pulses of 10 ns duration at a probing radiation wavelength of 355 nm have been established using the Z-scan method. Manifestations of the formation of hybrid nanostructures have been established using transmission electron microscopy and optical absorption and luminescence spectroscopy. The interaction of colloidal QDs and NPs was manifested as the recombination luminescence quenching of the former with a peak at a wavelength of 450-480 nm. For ensembles of colloidal $Zn_{0.5}Cd_{0.5}S$ QDs with an average size (2.0, 2.2, 2.4 nm), nonlinear refraction (defocusing) of 10 ns laser pulses in the near ultraviolet (355 nm) was established, the coefficient of which increased with increase in QDs. It has been established that during the interaction of $Zn_{0.5}Cd_{0.5}S$ QDs with Ag NPs, the suppression of nonlinear refraction was observed against the background of a twelvefold increase in the nonlinear absorption coefficient. It was concluded that the most probable reason for the observed changes in the nonlinear optical response is the polarizing effect of plasmonic Ag NPs.

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

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1. Introduction

The interaction of noble metal NPs and semiconductor colloidal QDs and dye molecules can significantly affect the optical properties of the latter [1, 2]. Recently, in the scientific literature there has been widespread interest in the study of hybrid nanostructures, characterized by the manifestation of plasmon-exciton interaction [3–9]. Such nanosystems are interesting from the point of view of controlling the luminescent, spectral and nonlinear optical properties of components due to the exchange of electronic excitations between QDs and Nps and the Rabi, Fano, and Purcell effects [1, 5, 6, 10–14]. The most attention is paid to the analysis of the manifestations of plasmon-exciton interaction in the spectral and luminescent properties of such nanosystems, while the nonlinear optical response remains practically unstudied, despite the prospect of their active use to control the intensity and phase of laser radiation [4, 5]. Theoretical studies propose models of plasmonic amplification of third-order nonlinear optical processes [15] and demonstrate the possibility of creating nanostructures with ultrafast response and the ability to reduce the size of nonlinear optical components [16]. In addition, there is evidence of a dielectric-metal hybrid system where an enhancement of optical nonlinearities is observed due to the strong coupling between the epsilon-near-zero mode in the indium tin oxide (ITO) nanofilm and the localized surface plasmon in the nanocavity [17]. The study revealed increases in the nonlinear refractive index and nonlinear absorption coefficient by three and two orders of magnitude compared to pure ITO, respectively. Plasmonic interaction is used to enhance such nonlinear processes as second harmonic generation and sum frequency generation [18]. An example of this is the experimental study [19], where the authors demonstrated the possibility of amplifying the output of the second harmonic generation signal of a Ti:Sapphire femtosecond laser on a nanosystem of gold nanoparticles with an average size of 80 nm in the presence of CdS quantum dots with an average size of 3 nm up to 20 times. The ratio of QDs to NPs was 200 to 1.

In addition to inorganic plasmon-exciton nanostructures, nanomaterials based on dyes and plasmonic nanoparticles have recently been considered promising in nonlinear optics [20]. There are several methods for modifying specified linear and nonlinear optical properties of organic dyes [21, 22]. One of the simplest and most effective methods is formation of the nanostructure with nanoparticles of noble metals. Plasmonic nanoparticles have unique optical characteristics resulting from localized surface plasmon resonances that generate intense electromagnetic fields near the nanoparticle surface and can interact with electronic transitions in nearby molecules such as organic dyes [23, 24]. Various studies have been reported on the modification of the electrical, chemical and optical properties of nanostructures based on organic dyes and metal nanoparticles; there are studies that consider the modification of the nonlinear optical response in such nanosystems [25, 26]. The driving force for these studies is the fact that the nanosystem acquires many unique optical properties compared to its components, since the presence of plasmonic nanoparticles affects the probabilities of optical transitions in organic dyes [27, 28]. The study [29] which demonstrates the enhancement of nonlinear refraction and nonlinear absorption of the organic dye Methyl Orange in the presence of silver and gold nanoparticles in the field of nanosecond pulses of the second harmonic generated by Nd^{3+}:YAG laser should be mentioned. Our study [4] is devoted to the investigation of such effects of the modification of nonlinear absorption of the solution of the Methylene blue dye in the presence of gold nanoparticles coated with a silicon oxide shell, where an increase in reverse saturable absorption in the dye was demonstrated. It should be noted that the number of studies considering the nonlinear optical response in the near ultraviolet range is small; mainly the properties of glasses and various nonlinear crystals are considered.

The goal of this study was to establish optimal conditions for the formation of hybrid nanostructures for nonlinear optical applications in the near ultraviolet. The nonlinear optical properties of $Zn_{0.5}Cd_{0.5}S$ quantum dots passivated with thioglycolic acid (QD $Zn_{0.5}Cd_{0.5}S$/TGA), with average sizes of 2.0, 2.2 and 2.4 nm in mixtures with silver nanoparticles (Ag NPs) of spherical geometry (10 nm) have been studied using the

Z-scan method. The samples were probed with third harmonic pulses generated by Nd^{3+}:YAG laser (355 nm) with a duration of 10 ns. In our study we used $Zn_{0.5}Cd_{0.5}S$ QDs, interesting because their exciton absorption peak is easily tuned by the synthesis and is located near the wavelength of the probing radiation (355 nm).

2. Experimental

The studied QDs and NPs samples were created using aqueous colloidal synthesis techniques. The $Zn_{0.5}Cd_{0.5}S$/TGA QDs were synthesized using an aqueous solution of zinc and cadmium nitrates in a ratio of 1 to 1. Then, with constant stirring, an aqueous solution of thioglycolic acid (TGA) was added to the reactor, and the formation of the Zn(Cd)-TGA complex was observed (the solution became cloudy, pH was 2.4). By adjusting the pH to 7 with an aqueous 0.1 M NaOH solution, the solution became transparent. Then an aqueous Na_2S solution, which is a source of sulfur was added. Molar ratios of precursors $\nu(TGA):n(Zn(NO_3)_2(Cd(NO_3)_2)):n(Na_2S)$ were 2:1:0.5 for quantum dots with an average size of 2.0 nm. The variation in the size of QDs was achieved by increasing the sulfur precursor ratio to 0.6 and 0.7, respectively, for QDs with sizes of 2.2 and 2.4 nm. Reaction products were removed from the QD colloidal solution by centrifugation with the addition of ethanol and re-dissolution in water in the original ratio. We estimated the ratio of Zn to Cd in the obtained QDs as 1 to 1; the provision of the more accurate estimate of the ratio of atoms using X-ray diffraction is a rather labor-intensive task due to the significant broadening of X-ray diffraction peaks from the studied nanocrystals. This has been demonstrated in many studies, including ours [5].

Silver nanoparticles of spherical geometry (Ag NPs) were obtained by the Turkevich method [30]. The method involves the reduction of silver ions Ag^+ from silver nitrate precursor $AgNO_3$ by sodium citrate ($Na_3C_6H_5O_7$). During the reduction process, clusters, and then nanoparticles stabilized by sodium citrate molecules are successively formed. The 20 ml of an aqueous solution of sodium citrate $Na_3C_6H_5O_7$ (4 mM) were added within 5 min into a boiling aqueous solution of silver nitrate $AgNO_3$ (1 mM) with a volume of 20 ml, followed by boiling and stirring for 30 min. The final solution had yellow color. Molar ratio of precursors in $\nu(AgNO_3):\nu(Na_3C_6H_5O_7)$ solution was 1:4. The resulting colloidal solution of silver nanoparticles was purified from reaction products by several cycles of deposition of Ag NPs on the bottom of test tubes during centrifugation and washing with distilled water. For the preparation of mixtures of the studied samples, a solution of Ag NPs was introduced into the QD solution in a ratio of about 1000 QDs to 1 NP.

The size of the studied QDs and NPs was determined by digital image analysis, using a Libra 120 transmission electron microscope (TEM) (CarlZeiss, Germany) with an accelerating voltage of 120 kV. The spectral and luminescent properties of the studied QDs, NPs and their mixtures were studied using USB2000+XR spectrometer (OceanOptics, USA) with a USB-DT radiation source (OceanOptics, USA). The luminescence spectra of $Zn_{0.5}Cd_{0.5}S$/TGA QDs was recorded under excitation with a 313 nm source (monochromatic mercury lamp radiation). The luminescence decay kinetics of QDs was measured using a TimeHarp~260 module (PicoQuant, Germany). The single photon 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.

The nonlinear optical properties of the samples were studied using the Z-scan method [31]. The setup and methodology are described in detail in [5].

Probing of the studied samples was carried out with pulsed laser radiation of the third harmonic of YAG:Nd^{3+} laser (LS-2132UTF, LOTIS TII) with a wavelength of 355 nm, a duration of 10 ns and a repetition rate of 1 Hz. The divergence of the laser beam was ensured by a converging spherical quartz lens with a focal length of 300 mm. The beam waist radius was ~30 μm. Samples of colloidal solutions in quartz cuvettes with the thickness of 1 mm were moved along the optical z axis of the collecting lens using a linear translator 8MT50-200BS1-MEn1 (Standa), from minus to plus z values, e.g. from the converging lens to the detector. The energy of the probing laser pulses was controlled by a PM100USB power and energy meter with an ES111C pyroelectric detector (Thorlabs) and amounted to 1.33 mJ.

3. Results and discussion

Digital analysis of TEM images of the initial components of QDs and NPs and their mixtures (Fig. 1) allows to determine the size and morphology of nanostructures. Thus, separate ensembles of $Zn_{0.5}Cd_{0.5}S$/TGA QDs were formed (2.0, 2.2, 2.4 nm) with a size dispersion of 20–30% (Fig. 1a-c). Ag NPs with spherical geometry had an average size of 10 nm (Fig. 1d).

In the optical absorption spectra of $Zn_{0.5}Cd_{0.5}S$/TGA QDs features associated with the most probable exciton transition at wavelengths of 320, 335 and 345 nm for QDs with an average size of 2.0, 2.2 and 2.4 nm (Fig. 2a) were observed. The light extinction spectrum of Ag NPs contained a plasmon resonance peak at a wavelength of 400 nm (Fig. 2a).

The absorption spectra of associates were a summation of the absorption spectra of QDs and the light extinction spectra of NPs (Fig. 2b). This finding indicates the absence of structural changes in the components during the formation of the associate. Luminescence spectra of $Zn_{0.5}Cd_{0.5}S$/TGA QDs were broad bands with maxima at 450, 473, 480 nm. A significant Stokes shift of 1.1 eV in the maximum of the luminescence band relative to the exciton absorption peak indicated the recombination nature of the luminescence. The situation with a noticeable offset of resonances in the absorption and luminescence of QDs and the light extinction of NPs was considered. A slight overlap of the light extinction spectra of NPs and luminescence of QDs will facilitate the exchange of electronic excitations between the components of QDs and NPs mixtures. Luminescence quenching by QDs by 3–4 times and acceleration of luminescence

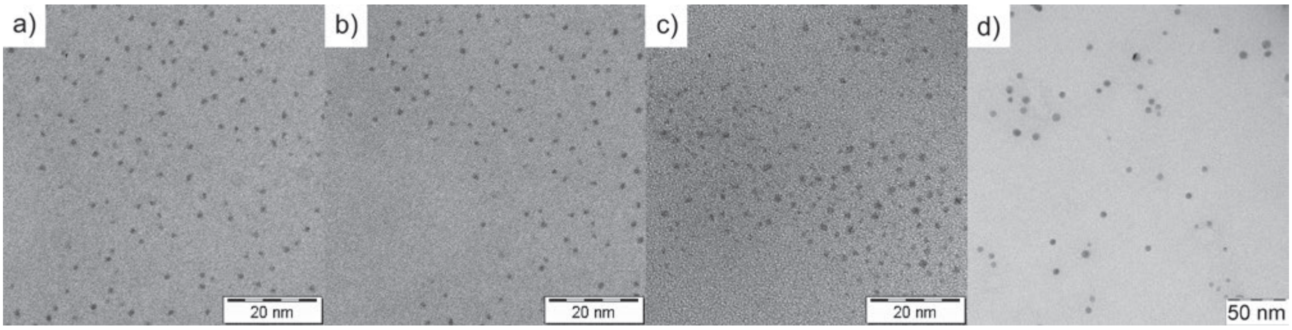

Fig. 1. TEM images of the studied $Zn_{0.5}Cd_{0.5}S$/TGA QDs samples with an average size of 2.0 nm (a), 2.2 nm (b), 2.4 nm (c) and silver nanoparticles of spherical geometry with an average size of 10 nm (d)

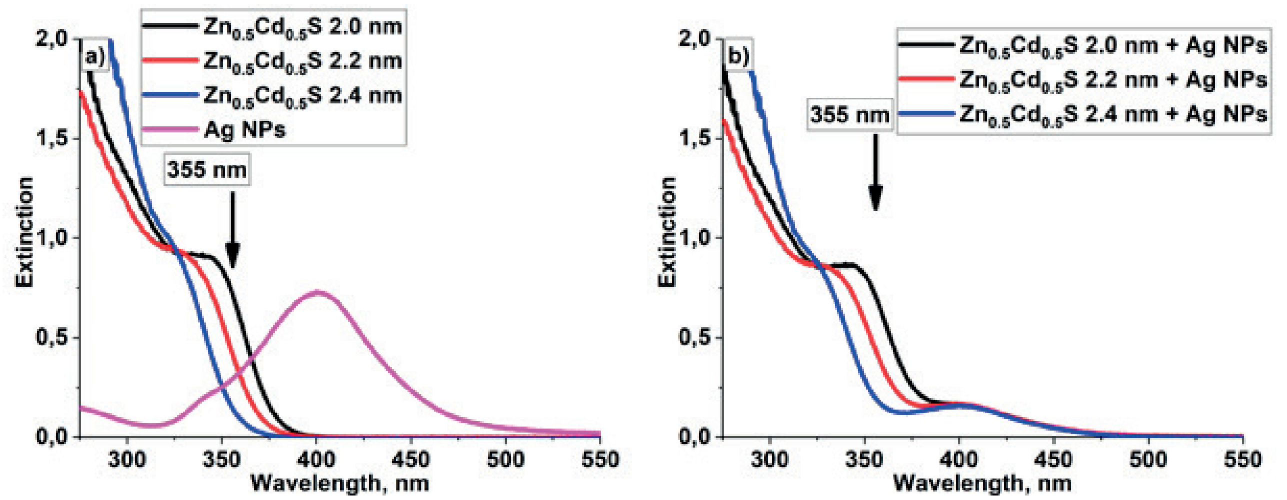

Fig. 2. Light extinction spectra of initial colloidal solutions of synthesized $Zn_{0.5}Cd_{0.5}S$/TGA QDs, Ag NPs (a) and their mixtures in a ratio of 1000 QDs to 1 NP (b)

decay kinetics by up to 2 times in mixtures with NPs indicated their interaction. Under the existing spectral conditions, two processes of exchange of electronic excitations can occur: nonradiative electronic excitation energy transfer from QDs to NPs and photoinduced charge transfer.

Under conditions of interaction between colloidal QDs $Zn_{0.5}Cd_{0.5}S$/TGA and AgNPs upon electronic excitation of one of the components, changes in the nonlinear optical response of a colloidal mixture compared to the response of individual components of the mixture. Using the Z-scan method using a scheme with a closed aperture, which allows recording nonlinear absorption and nonlinear refraction (beam divergence), suppression of nonlinear refraction and enhancement of nonlinear absorption were established QDs $Zn_{0.5}Cd_{0.5}S$/TGA in the presence of Ag NPs (Fig. 3b).

It is noteworthy that Z-scans of Zn $CT_{0.5}Cd_{0.5}S$/TGA exhibit profiles characteristic of defocusing laser probe pulses (Fig. 3a) and very weak nonlinear absorption. As the average QDs size increased, an increase in the level of nonlinear refraction was observed. Nonlinear refraction in QDs is realized due to the "band filling" [32, 33], and nonlinear absorption was associated with reverse saturable absorption (RSA), which occurred during transitions involving levels of localized states, including levels of luminescence centers.

In turn, for Ag NPs in Z-scans a dip in the focal plane associated with dynamic scattering was observed, which was confirmed by the signal on an additional photodiode located at an angle to the optical axis of the converging lens during Z-scanning.

An estimation of nonlinear refractive coefficients (γ) and nonlinear absorption (β) was performed by approximating the experimentally obtained dependences by the expression [34]:

$$T(z) = 1 + \frac{4x}{(x^2+9)(x^2+1)}\Delta\Phi - \frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\Psi,$$

where $x = z/z_0$, $z_0 = 0.5k(w_0)^2$, $k = 2\pi/\lambda$, w_0 – beam radius in the focal plane, λ – radiation wavelength, $\Delta\Phi = k\gamma I_0 L_{eff}$ and $\Delta\Psi = \beta I_0 L_{eff}/2$ – parameters describing the phase shift near the focal point, γ – nonlinear refractive index, β – nonlinear absorption coefficient, I_0 – intensity of laser radiation in the waist, $L_{eff} = (1 - \exp(-\alpha L))/\alpha$ – the effective thickness of the sample, α – the linear absorption coefficient, L – sample thickness. The values of the nonlinear refraction coefficient equal to $\gamma = -5.9\cdot10^{-16}$ cm^2 W^{-1} (2.0 nm); $\gamma = -7.2\cdot10^{-16}$ cm^2 W^{-1} (2.2 nm), $\gamma = -9.1\cdot10^{-16}$ cm^2 W^{-1} (2.4 nm) were established for $Zn_{0.5}Cd_{0.5}S$/TGA QDs of various mean sizes. The nonlinear absorption coefficient for all QD samples was no higher than $1.0\cdot10^{-11}$ cm W^{-1}.

The theoretical analysis of the contribution of thermal defocusing into nonlinear refraction was analyzed by analogy with study [35] by solving the heat equation. It was concluded that, under the conditions of our experiments, the time for the

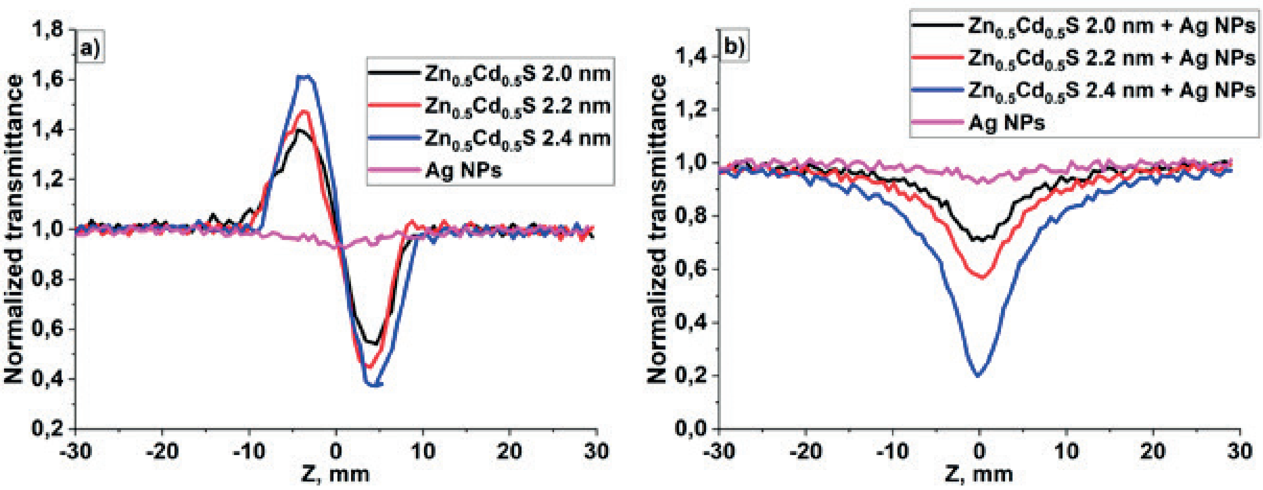

Fig. 3. Z-scans in closed-aperture geometry of the initial components of a $Zn_{0.5}Cd_{0.5}S$-based hybrid nanostructure and silver nanospheres (a) and their mixtures (b). Z-scans were obtained by probing the studied colloidal solution with laser pulses with a duration of 10 ns at a wavelength of 355 nm and a pulse energy of 1.33 mJ

implementation of a thermal lens in solutions of the studied samples was about ≈ 3.8 ms, which significantly exceeded the laser pulse duration of 10 ns. The low repetition rate of probing pulses of 1 Hz also prevented heat accumulation. An estimate of the nonlinear refractive index of the thermal conductivity equation indicated a value on the order of -10^{-19} cm^2 W^{-1}, which was two orders of magnitude lower than the value obtained experimentally. Thus, it can be established that thermal refraction does not influence the nonlinear optical response in our samples.

In addition to the calculations obtained above, the distance between the peak and the dip in the Z-scan with a closed aperture was analyzed and it was about 0.6 cm. This distance, according to the data of [36], allows to determine the predominant mechanism for defocusing laser radiation as follows: for a thermal lens the characteristic distance between the peaks in the Z-scan corresponds to the distance ΔZ ≈ 1.2z0 (z0 – Rayleigh length equal to 0.353 cm for the probe radiation length of 355 nm); for nonlinearities of higher orders, the corresponding distance was equal to ΔZ ≈ 1.7z0. These data were obtained by studying nonlinear refraction in CS_2 in the field of femtosecond pulses. Accordingly, the characteristic distances between the peak and the dip for the thermal nature of defocusing were equal to 0.42 and 0.56 cm for nonlinearities of higher orders. In this case, non-thermal nature of refraction in our experiments can be concluded.

It has been established that the lowest contribution to the nonlinear optical response from dynamic scattering was made by mixtures of QDs and NPs in a concentration ratio of 1000:1. Concentrations were estimated spectroscopically using literature data on molar extinction coefficients. Along with the disappearance of the nonlinear refraction of QDs in mixtures with NPs, an increase in the dip in the Z-scan in the focal plane of the lens, characteristic of nonlinear absorption, was observed, which, based on the analysis of the shape of the dependence of the energy of radiation transmitted through the sample on the energy of the incident radiation, was attributed to RSA. The analysis was performed by mathematical processing of Z-scans by analogy with [37], which allowed to establish a saturable dependence of the absorption coefficient of the studied samples on the intensity of the incident radiation, characteristic of reverse saturable absorption with the involvement of real QD states, while two-photon absorption was characterized by a linear dependence. With increasing QD size, an increase in the level of reverse saturable absorption was observed. This pattern can be explained by an increase in the number of broken bonds on the QD surface involved in the implementation of RSA with increasing QD volume. This assumption was confirmed by the results of [38], which showed a significant influence of surface broken bonds and defects in CuS quantum dots with an average size of 2–4 nm and 5–11 nm on the reverse saturable absorption. In this study the nonlinear optical response in a field of 100 fs laser pulses at a probe radiation wavelength of 800 nm was investigated. The nonlinear absorption coefficient increased up to 26 times with increase in size of CuS QDs. The study [39] provides experimental data on the effect of surface defects of PbS QDs on the nonlinear absorption and nonlinear refraction coefficients in the field of femtosecond laser pulses at a wavelength of 800 nm. It was shown that as the size of PbS QDs decreased from 4.3 to 1.5 nm, the ratio of the QD surface to volume increased sharply, which made the influence of surface traps even more pronounced and led to a further decrease in the nonlinear response. The authors noted that improved nonlinear optical response can be achieved by creating QDs with fewer defects, which will prevent capture of the charge into trap states and decrease the oscillator strength.

Based on the approximation of Z-scans, the values of the nonlinear absorption coefficient for the studied mixtures of $Zn_{0.5}Cd_{0.5}S$ QDs (2.0 nm) and Ag NPs were established – $\beta = 4.5\cdot10^{-11}$ cm W^{-1}; for mixtures of $Zn_{0.5}Cd_{0.5}S$ QDs (2.2 nm) and Ag NPs – $\beta = 6.6\cdot10^{-11}$ cm W^{-1}; for mixtures of $Zn_{0.5}Cd_{0.5}S$ QDs (2.4 nm) and Ag NPs – $\beta = 12.3\cdot10^{-11}$ cm W^{-1}. Thus, an increase in the nonlinear absorption coefficient of mixtures of QDs and NPs up to 12 times compared to free $Zn_{0.5}Cd_{0.5}S$/TGA QDs was revealed.

The enhancement of RSA in QDs and NPs mixtures indicated the participation of local states in the formation of nonlinear absorption, which were most likely determined by broken bonds on the QD surface. Accordingly, optical transitions involving these states in the presence of plasmonic NPs can lead to a change in the probability ratio of two-step optical transitions that determine RSA [40]. In this case, a redistribution of the population of local states of the QD in the field of laser pulses is probable, which can lead to the suppression of the effect of nonlinear refraction caused initially by the "band-filling" effect and a change in the refractive index of the colloidal solution in accordance with the Kramers-Kroning relation [31]. The probabilities of the corresponding transitions can change under the polarizing action of NPs, which affects the nonlinear optical response (an increase in nonlinear optical absorption) regardless of the settings of the optical resonances (luminescence peak and plasmon peak, respectively). At the same time, the observed pattern in nonlinear optical and spectral luminescent properties can also arise during photostimulated charge transfer between the components of QDs and NPs mixtures.

4. Conclusions

Control of the nonlinear optical response of $Zn_{0.5}Cd_{0.5}S$/TGA QDs associated with Ag NPs of spherical geometry in the radiation field of laser pulses (10 ns) with a wavelength of 355 nm using spectral-luminescent methods and the Z-scanning method has been demonstrated. The predominant mechanism for the implementation of the nonlinear optical response in the studied samples has been established: nonlinear absorption is realized due to reverse saturable absorption, self-focusing was of a non-thermal nature and was associated with the "band filling". The mixtures of $Zn_{0.5}Cd_{0.5}S$/TGA QDs and Ag NPs of different mean sizes were characterized by suppression of nonlinear refraction and enhancement of nonlinear absorption by up to 12 times, which can find practical application in the production of passive optical power limiters in the near ultraviolet.

Author contributions

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