DOI 10.1007/s10946-024-10191-9
Journal of Russian Laser Research, Volume 45, Number 1, January, 2024

NONLINEAR OPTICAL PROPERTIES OF PLASMON–EXCITON NANOSTRUCTURES BASED ON PbS QUANTUM DOTS AND GOLD NANORODS IN THE FIELD OF NANOSECOND LASER PULSES

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Abstract

We present the results of our study of nonlinear optical response observed in plasmon–exciton nanostructures based on PbS quantum dots passivated with thioglycolic acid and gold nanorods under the influence of 10 ns second harmonic pulses (532 nm) of $\mathrm{Nd}^{3+}:\mathrm{YAG}$ laser. We show that the association of components of a hybrid nanostructure leads to increase in the reverse saturable absorption in PbS quantum dots against the background of nonlinear refraction. Coating quantum dots with a monolayer of SiO_2 reduces this effect due to blocking the process of phototransfer of charge from a quantum dot to a metal nanoparticle, which is confirmed by the quenching and reduction in the luminescence lifetime of PbS quantum dots in the presence of gold nanorods.

Keywords: plasmon–exciton nanostructure, colloidal quantum dots, PbS, plasmonic nanoparticle, nonlinear refraction, nonlinear absorption, reverse absorption saturation.

1. Introduction

The presence of noble metal nanoparticles near quantum dots (QDs) can significantly affect the optical properties of the latter [1, 2]. Recently, there has been active research into nanosystems with the plasmon–exciton interaction based on metal nanoparticles (NPs) and dye molecules [3, 4], quantum dots and NPs [5–9]. Such systems are interesting due to the possibility of controlling the luminescent, spectral, and nonlinear optical properties of the components of the nanosystem due to the exchange of electronic excitations between QDs and NPs, the Fano and Purcell effects [1, 5, 6, 10–14]. Basically, in the scientific literature, the main emphasis is placed on the manifestation of plasmon–exciton interaction in the spectral and luminescent properties of such nanosystems. An urgent task is to establish the conditions for the formation of nanostructures with plasmon–exciton interaction based on quantum dots and plasmonic nanoparticles that provide unique nonlinear optical properties [5].

In this work, we study nonlinear optical properties of PbS quantum dots (QDs) passivated with thioglycolic acid, with an average size of 3.5 nm, and the same QDs coated with a monolayer of SiO_2 in the presence of gold nanorods (NRs) (4×25 nm), using the Z-scan method. The peak of the longitudinal

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Manuscript submitted by the authors in English on November 21, 2023.

plasmon resonance of Au NRs (915 nm) corresponds to the absorption feature of PbS QDs (913 nm) associated with the first excitonic transition in the QD. In this way, the tuning of resonances in the absorption of QDs is provided and the extinction of NRs is achieved; that is, optimum conditions are created for the exchange of electronic excitations between the components of the hybrid nanostructure.

2. Materials and Methods

Colloidal PbS/TGA QDs are synthesized in water using an original method developed by our team. Thioglycolic acid (TGA) is used as a passivator, Na_2S is the source of Sulfur, and $Pb(NO_3)_2$ is the lead precursor. 0.210 ml of TGA is poured into 250 ml of an aqueous solution of $Pb(NO_3)_2$ (6 mM), with constant stirring. The solution becomes cloudy, then the pH is adjusted to 11, using a NaOH solution (0.1 M), and the solution becomes clear. Next, an aqueous solution of Na_2S (7.7 mM) is added to the reactor in the following volumes of 60 ml. In this way, we obtain PbS QDs. The ratio of the molar concentrations of $C_{S-}/C_{\mathrm{Pb}+}$ in the reactor for the obtained samples is 0.43. To remove reaction products after synthesis, QDs are precipitated by centrifugation with the addition of ethanol and redispersed in water. The pH of the final QD solutions is 7.2.

We determine the size of the studied QDs, using a Libra 120 transmission electron microscope (TEM) (CarlZeiss, Germany) with an accelerating voltage of 120 kV. Digital analysis of TEM images shows the formation of ensembles of PbS QDs, with an average size of 3.5 nm. The dispersion in the size of quantum dots is 10–15%.

To establish the possibility of controlling the nonlinear optical response of QDs by reducing the probability of charge transfer, PbS QDs are coated with a monolayer of SiO_2, an original technique developed by our team [15]. To grow a monolayer of SiO_2 on the surface of PbS QDs, the following original technique is used. NaOH solution (0.1 M) is added to 40 ml of PbS QD solution with constant stirring to bring the pH to 11.2. Next, 10 ml of an aqueous solution of (3-Mercaptopropyl)trimethoxysilane (MPTMS) (5 mM) is added to the resulting solutions of PbS QDs with constant stirring. Then they are stirred for 24 h., and the solutions are freed from reaction products by centrifugation with the addition of ethanol and redispersed in water. TEM images of PbS/MPTMS QDs (hereinafter referred to as PbS/SiO_2 QDs) are obtained again. Size analysis shows that the PbS QD does not change during the growth of the SiO_2 monolayer. The presence of a SiO_2 monolayer is confirmed by energy dispersive X-ray analysis (EDX), using a spectrometer built into the TEM Libra 120 PLUS (Carl Zeiss, Germany). The analysis of EDX results is described in detail in [16, 17].

Multistage colloidal synthesis is used to form gold nanorods (Au NRs) [18]. An aqueous solution of the surfactant cetyltrimethylammonium bromide (CTAB) is used to grow cylindrical NRs, being both a weak reducing agent and an anisotropic medium. Initially, a seed solution of gold nanospheres, with a size of 3 nm, was prepared by reducing aqueous chlorauric acid $HAuCl_4$ (7 μl, 0.36 mol) with a solution of $NaBH_4$ (1.0 ml, 5 mmol) in an aqueous solution of CTAB (20 ml, 0.02 mmol). Anisotropy of NRs growth is ensured by introducing a mixture of $HAuCl_4$ (28 μl, 0.36 mol), CTAB (50 ml, 0.1 mmol), silver nitrate ($AgNO_3$)(0.1 ml, 0.02 mol), and ascorbic acid ($C_6H_8O_6$) (5 ml, 0.05 μmol). The addition of $AgNO_3$ helps to control the length-to-diameter ratio of Au NRs. According to the results of digital processing of TEM images, the average size of gold nanorods is 4×25 nm.

We record optical absorption and luminescence spectra, using a USB2000+ spectrometer (Ocean Optics, USA) with a USB-DT radiation source (Ocean Optics, USA). Measurements of the QDs luminescence decay kinetics are carried out, using the TimeHarp∼260 module (PicoQuant, Germany), which operates in the single photon counting mode. The detector is an InGaAs SPAD (MPD), with a time resolution of 0.2 ns. The luminescence decay curves are approximated by a theoretical curve, using a deconvolution procedure with the experimentally measured response function of the equipment.

To study the nonlinear optical properties, we use the Z-scanning technique [19], which consists of measuring the normalized transmittance of the sample under study, as it moves relative to the focal plane of the collecting lens along the optical z axis. The normalized transmittance is defined as the ratio of the transmittance of the sample $T(z)$ at a point with coordinate z to the transmittance of the sample in the linear mode at low intensity, away from the focus of the collecting lens T ($z \to \infty$). In this way, we measure the transmittance of the sample at different cross sections of the size of the Gaussian beam (various intensities); that is, the sample is actually scanned according to the intensity of the laser radiation. The experiments used the second harmonic radiation of a $\mathrm{Nd}^{3+}:\mathrm{YAG}$ laser (LS-2132UTF, LOTIS TII) with a radiation wavelength of 532 nm, a duration of 10 ns, and a repetition rate of 1 Hz. The radiation is focused by a spherical lens with a focal length of 300 mm. Quartz cuvettes, 5 mm thick, containing the samples under study, are 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 is ~30 μm.

The setup was described in detail in [20]. Measurements are carried out using pulse energies of 0.16 mJ, which are monitored by a PM100USB power and energy meter and ES111C detector (Thorlabs).

3. Results and Discussion

We select the samples under study, taking into account the precise tuning of resonances in the absorption of PbS QDs and the extinction of Au NRs; see Fig. 1 a. In PbS quantum dots, it is difficult to distinguish feature in absorption at a wavelength of 913 nm, associated with the first excitonic transition in the QD. The absence of a pronounced feature in the absorption of QDs is due to the high scatter in QD sizes. To determine the position of the exciton transition, luminescence excitation spectra are used, with the signal recorded at the maximum of the luminescence band; see Fig. 1 a inset. The gold nanorods

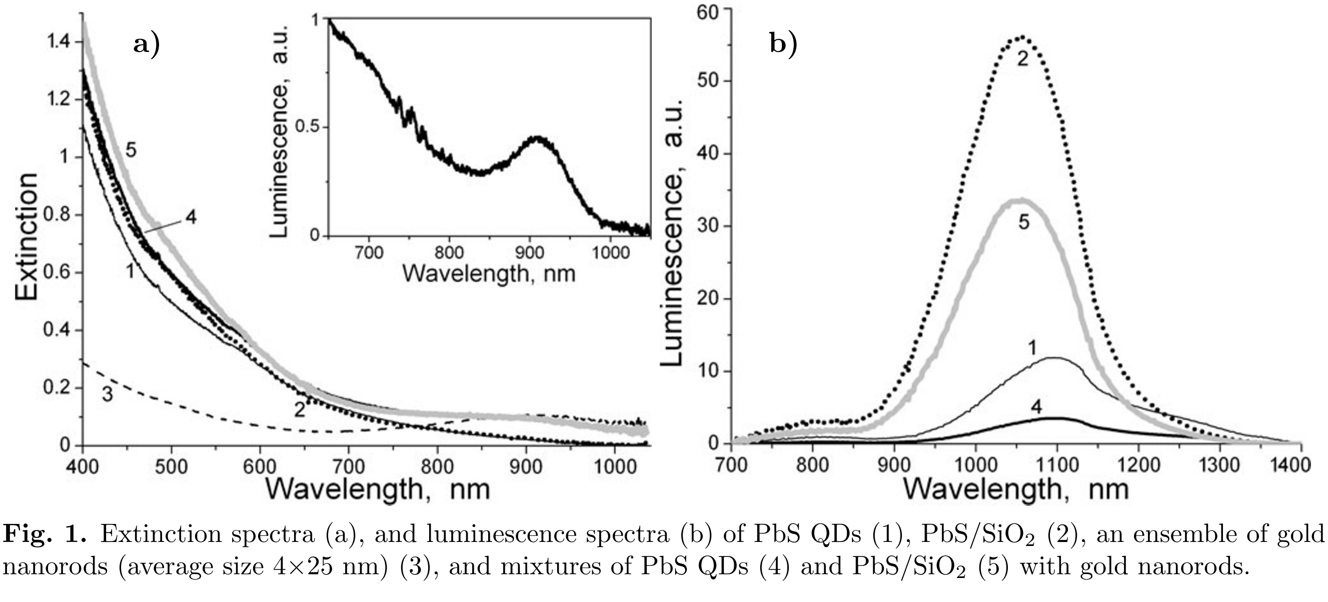

Fig. 1. Extinction spectra (a), and luminescence spectra (b) of PbS QDs (1), $\mathrm{PbS/SiO_2}$ (2), an ensemble of gold nanorods (average size 4×25 nm) (3), and mixtures of PbS QDs (4) and $\mathrm{PbS/SiO_2}$ (5) with gold nanorods.

exhibit an extinction peak at 915 nm, associated with the longitudinal plasmon resonance in the NPs. Mixtures of the studied samples do not show significant changes in the extinction spectra and are the sum of the extinctions of the components of the nanostructure. Coating PbS QDs with a monolayer of SiO_2 does not affect the linear absorption properties of the sample. It is worth noting that the application of a monolayer of SiO_2 to the surface of a QD leads to increase in the luminescence intensity up to 4.5 times compared to the original QDs (Fig. 1 b) and increase in the luminescence lifetime up to 1.3 times (Fig. 2) from 1200 to 1530 ns. This approach ensures passivation of dangling bonds on the surface of QDs, which can be channels for non-radiative recombination of electronic excitations, as evidenced by increase in the luminescence lifetime [15].

The addition of gold nanorods to a solution of PbS QDs manifests itself in the quenching of QDs luminescence by a factor of 3 and the acceleration of the luminescence lifetime by a factor of 2.5. The hybrid structure based on PbS/SiO_2 QDs demonstrates quenching of QDs luminescence in the presence of NRs by 1.7 times and acceleration of kinetics by 1.5 times; see Fig. 2. The above data indicate that charge transfer is the most likely process for the exchange of electronic excitations.

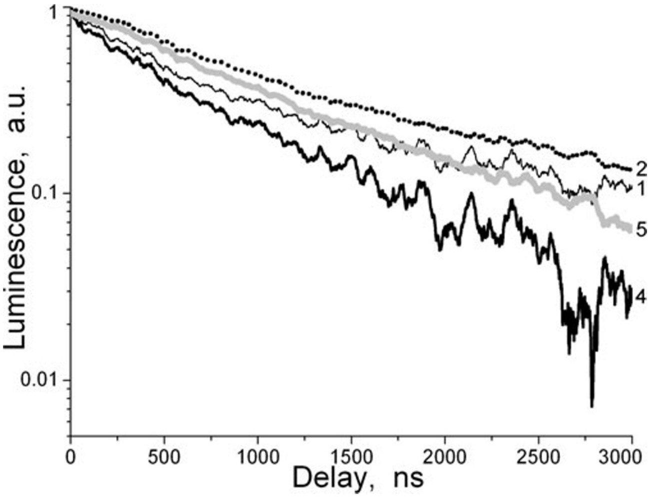

Fig. 2. Decay of luminescence of the samples under study with the same notation as in Fig. 1.

Let us turn to the nonlinear optical properties of the samples under study. The colloidal solution containing gold nanorods does not demonstrate a nonlinear optical response under our experimental conditions; see Fig. 3. Z-scans of PbS and PbS/SiO_2 QDs obtained in a closed-aperture geometry demonstrate defocusing of laser radiation. It is manifested in a symmetrical relative to the focal plane of the collecting lens increase in the transmission of the sample due to a decrease of the divergence of the probe radiation ($z < 0$) and a decrease of the transmission of the sample, due to increase in the divergence of the probe radiation ($z > 0$); see Fig. 3. In this case, the predominant mechanism of nonlinear refraction is the effect of filling states ("band filling" [21–23]). It is worth noting that coating PbS QDs with a monolayer of silicon dioxide has virtually no effect on nonlinear absorption and refraction in comparison with the original QDs. The mechanism of nonlinear absorption in the QDs under study is the reverse saturation absorption on localized states of QDs defects [15].

The introduction of plasmonic gold nanorods into a solution of PbS QDs changes the nonlinear optical response of PbS QDs – against the background of nonlinear refraction, increase in the nonlinear absorption is observed. Moreover, in the case of PbS/SiO_2 QDs, the magnitude of the dip in the Z-scan is 1.3 times smaller than in the case of unmodified QDs.

To estimate the coefficients of nonlinear absorption and nonlinear refraction, we approximate the experimentally obtained Z-scans by the expression [24]

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

where $x = z/z_0$, $z_0 = 0.5\,k(w_0)^2$, $k = 2\pi/\lambda$, w_0 is the beam radius in the focal plane, λ is the radiation wavelength, $\Delta\Phi = k\gamma I_0 L_{\text{eff}}$ and $\Delta\Psi = \beta I_0 L_{\text{eff}}/2$ are parameters describing phase shift near the focal

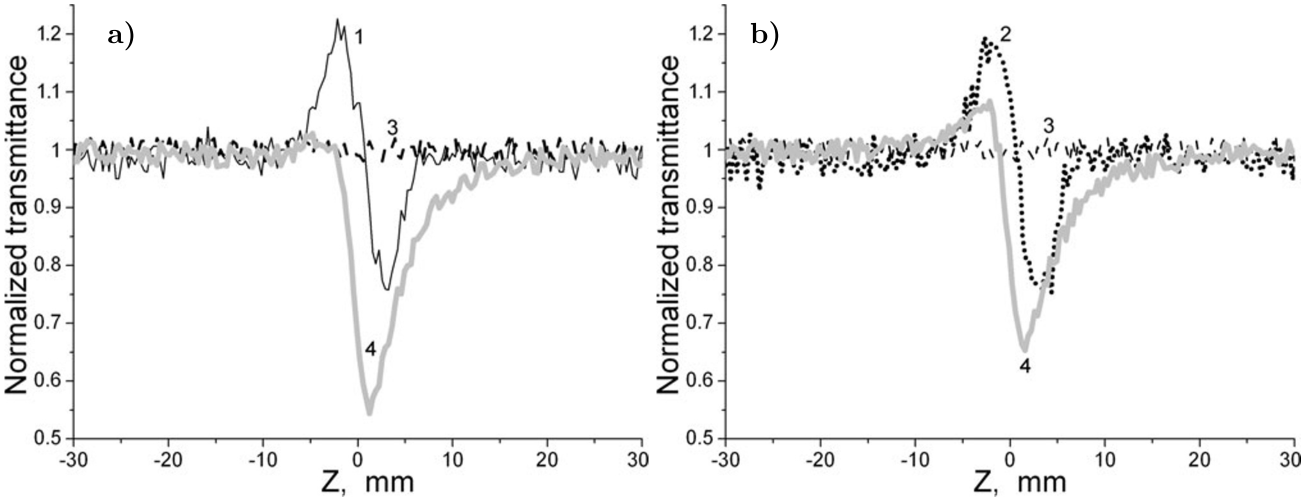

Fig. 3. Z-scans in closed aperture geometry of PbS QDs (curve 1) and gold nanorods (curve 3) and a hybrid nanostructure of them (curve 4) (a) and PbS/SiO$_2$ QDs (curve 2) and gold nanorods (curve 3) and a hybrid nanostructure of them (curve 5) (b). Samples of the colloidal solutions under study are probed by laser pulses with a duration of 10 ns, at a wavelength of 532 nm.

point, γ is the nonlinear refractive index, β is the nonlinear absorption coefficient, I_0 is the intensity of laser radiation in the waist, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient, and L is the sample thickness.

The following nonlinear refraction (γ) and absorption (β) coefficients are determined:

PbS (PbS/SiO$_2$), $\gamma = -4.5 \cdot 10^{-15}$ cm$^2 \cdot$ W^{-1}, and $\beta = 8.2 \cdot 10^{-11}$ cm $\cdot$ W^{-1};

mixture of PbS + Au NRs, $\gamma = -4.3 \cdot 10^{-15}$ cm$^2 \cdot$ W^{-1}, and $\beta = 5.1 \cdot 10^{-10}$ cm $\cdot$ W^{-1};

mixture of PbS/SiO$_2$ + Au NRs, $\gamma = -4.4 \cdot 10^{-15}$ cm$^2 \cdot$ W^{-1} and $\beta = 2.9 \cdot 10^{-10}$ cm $\cdot$ W^{-1}.

It is clearly seen that, in the case of PbS QDs with a modified SiO$_2$ surface, there is a smaller increase in the nonlinear absorption coefficient (3.5 times) compared to the original PbS + Au NRs QDs (6.2 times). This indicates the possibility to control the nonlinear optical parameters of a plasmon–exciton nanosystem by spatial separation of components and/or passivation of dangling bonds on the QD surface involved in the exchange of electronic excitations between the QD and metal nanoparticles. This is indirectly evidenced by the quenching of QD luminescence in the presence of gold nanorods and the acceleration of decay, which was discussed above.

In our experiments, tt is worth noting separately that the contribution to the nonlinear optical response of hybrid nanostructures and their dynamic scattering components is small. This is confirmed by recording the signal on an additional photodiode located at an angle to the optical axis of the collecting lens during Z-scanning. This is achieved by selecting the optimum ratio of QDs to gold nanorods of the order of 1000 QDs to 1 NPs.

4. Conclusions

In the work, we demonstrated the possibility of controlling the nonlinear optical absorption of PbS QDs passivated with thioglycolic acid in the presence of gold nanorods by depositing a monolayer of SiO$_2$ on the QDs, which led to a decrease of the influence of plasmon–exciton interaction on the luminescent and nonlinear optical properties of the QDs. The samples were probed with pulsed laser radiation with a wavelength of 532 nm and a duration of 10 ns, using the Z-scan technique. By approximating Z-scans, it was possible to establish an increase the nonlinear absorption coefficient of PbS QDs in the presence of gold nanorods from 3.5 times with a SiO_2 shell to 6.2 times (without modification of the QDs surface) relative to the original QDs.

Acknowledgments

The work was supported by the Russian Science Foundation under Grant No. 22-22-00842.

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