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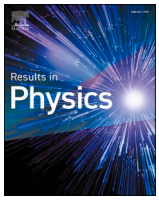

Optical gain appearance in the CdSe/CdS nanoplatelets colloidal solution

Alexander M. Smirnov [a,b,*], Anastasia D. Golinskaya [a], Vladimir N. Mantsevich [a], Maria V. Kozlova [a], Kseniia V. Ezhova [c], Bedil M. Saidzhonov [d], Roman B. Vasiliev [d], Vladimir S. Dneprovskii [a]

[a] Lomonosov Moscow State University, Faculty of Physics, Chair of Semiconductors and Cryoelectronics and Quantum Technology Center, Moscow, Russia
[b] Kotelnikov Institute of Radioengineering and Electronics of RAS, Moscow, Russia
[c] Faculty of Engineering Research, ITMO University, St. Petersburg, Russia
[d] Lomonosov Moscow State University, Faculty of Materials Science, Moscow, Russia

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ABSTRACT

The experimental investigations of the colloidal heterostructured CdSe/CdS nanoplatelets transient absorption in the regime of one-photon stationary excitation of excitons by high-intensity nanosecond laser pulses are presented. A strong dependence of exciton's transitions behavior on nanoplatelets concentration in colloidal solution and pump intensities was studied for the first time. The revealed nonlinear transmission changes of the nanoplatelets solutions with different optical density were explained by the presence of phase space filling effect, energy exchange between exciton states, reabsorption processes and exciton–exciton interaction. The most vital result of the paper is the identification of conditions for the existence of the optical gain in colloidal solutions of nanoplatelets.

Introduction

Semiconductor nanocrystals are quantum-confined objects with carriers motion being restricted in one, two or three directions. Among the most studied semiconductor nanocrystals are CdSe-based structures [1–3] due to their very promising potential application in the optoelectronic devices operating in the visible spectrum such as light-emitting diodes [4], solar cells [5], sensors [6] and other optoelectronic systems [7,8]. Significant attention is paid to the nanocrystals nonlinear optical properties research [9,10]. Electronic and optical properties of semiconductor nanocrystals can be successfully tuned by varying the size, morphology, lattice strain, capping shells, surface engineering and control under dimensionality [11–14]. Among all quantum-confined CdSe-based materials, two-dimensional atomically ultrathin nanosheets, i.e. nanoplatelets [15,16], attract strong attention due to their unique optical and electronic properties. In nanoplatelets the carriers are spatially confined within a finite thickness of the nanocrystal and freely move in the plane of the nanoplatelet. Nanoplatelets demonstrate a number of remarkable physical properties. Their optical resonance can be tuned due to the size quantization in one direction [15,16]. The binding energy of excitons in nanoplatelets is of the order of few hundreds of meV [17,18], which makes excitonic resonances visible at room temperature [19]. Moreover, the surfaces of nanoplatelets are atomically flat, so the excitonic lines are very sharp, the inhomogeneous broadening is absent [19]. So, nanoplatelets reveal giant oscillator strength, ultrashort radiative fluorescence lifetime and large linear/nonlinear absorption cross-sections [17,18]. Considering the extremely high surface to volume ratio, the practical application of nanoplatelets usually requires the creation core/shell [19], core/crown [20] or core/crown/shell [21] heterostructures. Heterostructured nanoplatelets are considered to be promising candidates for optical gain and lasing applications [22–24]. The realization of the optical-gain regime in semiconductor planar nanocrystals is a complicated challenging task involving the detail understanding of such processes as: Auger recombination, carriers trapping, photoinduced absorption and exciton bleaching. Additionally, the improvement of optical gain properties of colloidal nanoplatelets strongly depends on nanoplatelets lateral size, concentration in colloidal solution and optical density. To the best of our knowledge, the investigation of nanoplatelets optical gain properties was previously performed only for pure CdSe-based structures without shell [25], and was not studied for heterostructured nanoplatelets.

The possibility to get optical gain in the colloidal nanostructures is very appealing, however, there are still no results demonstrating the

* Corresponding author.
E-mail address: alsmir1988@mail.ru (A.M. Smirnov).

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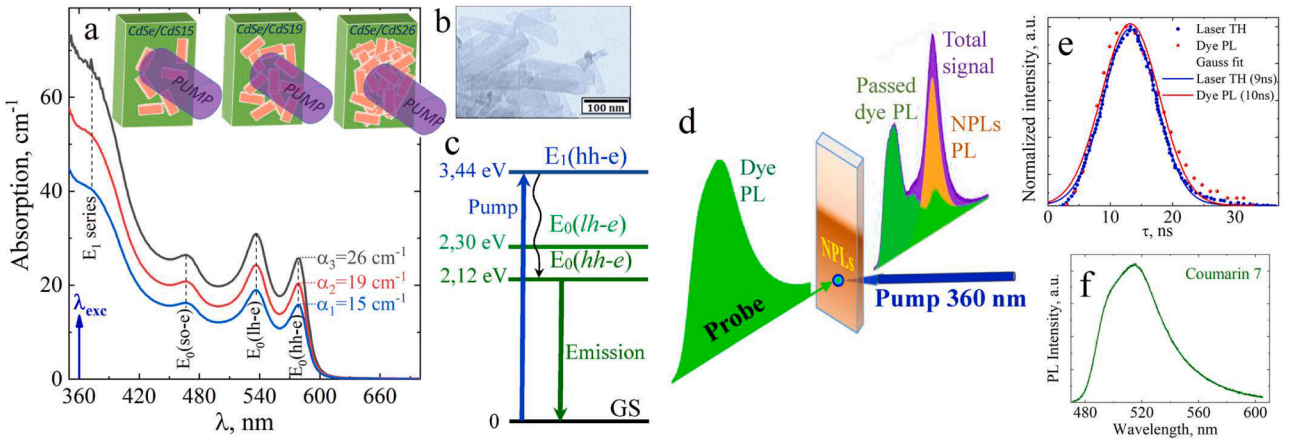

Fig. 1. a) The linear absorption spectra of the solution with low (blue line), moderate (red line), and high (black line) concentration of nanoplatelets. The inset shows the visual sketch of CdSe/CdS15, CdSe/CdS19 and CdSe/CdS26 samples. b) The TEM-image of the nanoplatelets. c) The scheme of the energetic scenario in the nanoplatelets and the excitonic transitions. d) The sketch of the measurement pump and probe procedure. e) The temporal profiles of the pump third harmonic pulse (blue dots) and the probe pulse (red dots). The curves show the corresponding Gaussian fits. f) Spectrum of the probe pulse, being the photoluminescence spectra of Coumarin-7.

appearance of optical amplification in colloidal solutions with concentration changing of the nanoplatelets.

In this paper the nonlinear transmission of colloidal CdSe/CdS core/shell nanoplatelets with different optical density is studied in the regime of one-photon stationary excitation of excitons at the different pump intensities. The most striking result of the paper is the experimental demonstration of the optical gain in colloidal solutions of semiconductor nanoplatelets.

Experiment and samples

Core-shell CdSe/CdS nanoplatelets have a 3,5 monolayer thick CdSe core and two monolayers of CdS shell on each basal plain of nanoplatelet. The growing procedure is described in details in Ref. [26]. Low-resolution transmission electron microscopy image (TEM) of the nanoplatelets demonstrates two-dimensional morphology (see Fig. 1b). Rectangle core–shell nanoplatelets with lateral sizes 35x100 nm^2 are dissolved in N-methylformamide solvent transparent in the visible spectral range. The studied solutions were prepared by adjusting the absorbance (optical density) of the colloidal nanoplatelets at the first exciton absorption peak. The nanoplatelets colloidal solutions were prepared in a 1 mm optical length cell at the room temperature. The solutions with different optical densities were prepared by the solvent dilution such that the optical absorbance near the first peak decreased approximately by a factor of 1,3 (Fig. 1a).

In the visible spectrum range, the absorption spectra of the nanoplatelets exhibit three well-resolved maxima attributed to excitons series E_0 at the Γ point of the Brillouin zone [27]. The maxima are centred at the wavelengths 466 nm, 538 nm and 580 nm corresponding to the exciton's transitions from the spin-orbital holes, light holes and heavy holes sub-bands to the conduction band [E_0(so-e), E_0(lh-e) and E_0(hh-e), respectively]. In the ultraviolet spectrum range, absorption spectra reveal a wide band centered approximately at 370 nm associated with the E_1 series of the high-energy exciton's transitions, originating from the X point of the two-dimensional Brillouin zone [27]. The observed single wide ultraviolet band appears as a superposition of the several excitons transitions from E_1 series. All the colloidal solution with different concentration of the nanoplatelets reveal nearly the same lh-e and hh-e exciton's transition energies. In the following, we will denote CdSe/CdS15, CdSe/CdS19 and CdSe/CdS26 samples with optical densities $\alpha_1 = 15cm^{-1}$, $\alpha_2 = 19cm^{-1}$, and $\alpha_3 = 26cm^{-1}$, correspondingly, at the wavelength of hh-e exciton's transition as the sample with low, moderate, and high concentration of the nanoplatelets, respectively (see Fig. 1a). Fig. 1c shows the energetic scenario in the nanoplatelets and the excitonic transitions [27–29]. The exciton states designated as E_0 and E_1 correspond to the transitions from the same sub-band of the heavy holes to the conduction sub-band corresponding to different points of the Brillouin zone (BZ) [27,30]. Thus, the excitation occurs for optical transitions associated with the X point of the two-dimensional BZ (state E_1), and relaxation by exciton-phonon interaction to the state E_0 comes from which the radiative recombination of excitons. The electrons are delocalized in the core and shell of CdSe/CdS nanoplatelets [28] due to the small difference (20 meV) between the conduction bands bottoms in CdS and CdSe. Heavy hole and light hole sub-bands are localized in the NPLs core as the difference between the tops of the valence bands in CdS and CdSe is about 0.7 eV.

The transmission changing was measured in the visible range (from 500 nm to 630 nm) by means of the pump and probe technique. The details of the experimental technique are reported in details in Ref. [31]. The sketch of the measurements procedure is shown in Fig. 1d. Briefly, the pumping was realized by the third harmonic of mode-locked Nd^{3+}: YAP laser pulses (blue arrow in Fig. 1d). The pump pulses resonantly excited the high-energy excitonic states of E_1 series (the wavelength 360 nm, pulse duration about 9 ns). The pump power varied from 60 kW/cm^2 to 2.4 MW/cm^2 by the set of neutral optical filters. Importantly, the duration of the pulses (9 ns) exceeded by the exciton generation, relaxation and recombination times in core/shell nanoplatelets, which is typically about few nanoseconds [32]. This allowed us to study one-photon stationary excitation regime. The broad spectrum of the probe light covers the wavelengths from 460 nm to 630 nm by Coumarin-7 dye photoluminescence (see green area in Fig. 1d and f for the spectrum of Coumarin-7). The probe light spectrum covers both exciton transitions spectrum and its duration (about 10 ns) coincides with the duration of the pump pulse. The probe pulse overlaps with the pump pulse (see Fig. 1e). At equal energies of excitation pulses the shape of the spectrum and the intensity of Coumarin-7 photoluminescence were preserved. The initial photoluminescence spectrum of the dye was compared with the photoluminescence spectrum of the dye passed through the sample. All spectra were measured by means of the SpectraPro 2300i spectrometer with PIXIS 256 CCD-camera. When plotting nonlinear transmission spectra, the own photoluminescence of the nanoplatelets (see orange area in Fig. 1c) was subtracted from recorded signal (see violet area in Fig. 1c).

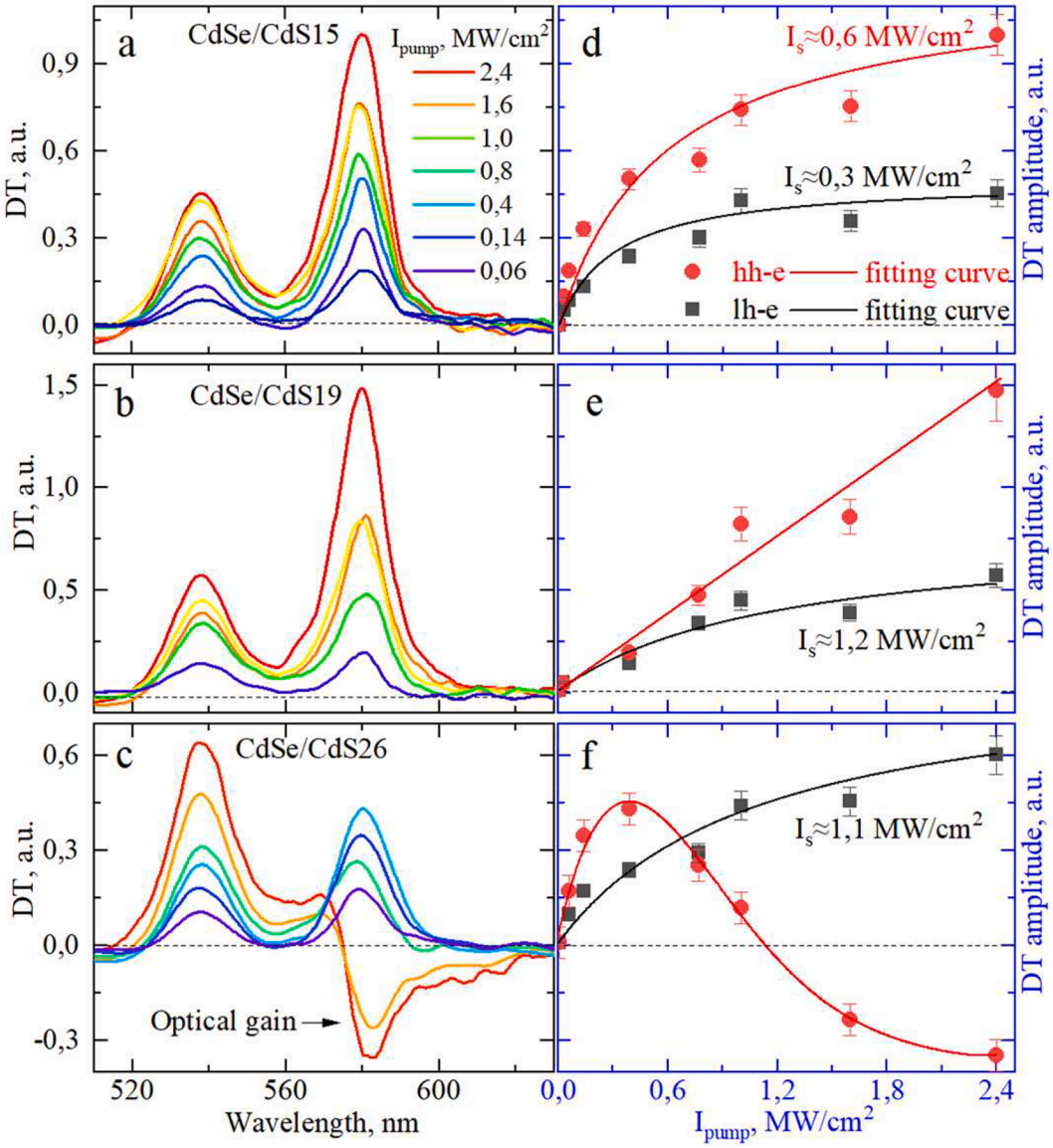

Fig. 2. Differential transmission spectra at the different pump intensities for the solution with low (a), moderate (b) and high (c) concentration of nanoplatelets. The amplitude of the DT maxima as a function of pump intensity for lh-e (black squares) and hh-e (red dots) exciton's transitions for the solution with low (d), moderate (e) and high (f) concentrations of nanoplatelets.

Results and discussions

To compare the transmission of the sample with and without pumping, we introduce the differential transmission (DT) at given wavelength: $DT = (T - T_0)/T_0$, where T_0 and T is the linear and nonlinear transmission of the solution, respectively. The DT spectra of the solutions with different nanoplatelets concentration for different on pump intensities are shown in Fig. 2(a–c).

The nonlinear transmission strongly depends on the optical density of the colloidal solution. The two pronounced peaks in the DT spectra of low- and moderate-concentrations of nanoplatelets in colloidal solutions (samples CdSe/CdS15 and CdSe/CdS19) correspond to the lh and hh excitons (see Fig. 2a and 2b, respectively) and reveal bleaching of lh-e and hh-e exciton's transitions. The excitons transitions bleaching occurs due to the dominating exciton's states filling effect accompanied by the transfer between hh and lh exciton's states [33,34].

For the high-concentration of nanoplatelets in colloidal solution (sample CdSe/CdS26) one can see that both lh-e and hh-e exciton's transitions reveal well pronounced bleaching only for pump intensities lower than $1 MW/cm^2$ (see Fig. 2c). For higher pump intensities lh-e exciton's transitions continue demonstrating positive DT, while hh-e exciton's transitions reveal well pronounced negative DT. The negative DT-signal corresponds to the optical gain regime provided by efficient reabsorption processes within the media. An effective re-emission processes competing with intrinsic nonradiative Auger effect provide the appearance of optical gain regime in colloidal solution with high concentration of nanoplatelets. It should be noted that the nanocrystals aggregation does not appear as exciton's transition energies are not changing with the concentration of nanoplatelets in colloidal solutions. We should mention that despite the observation of well pronounced negative DT-signal in CdSe/CdS26 sample, the stimulated emission was not observed for the used pump intensities. The existence of optical gain is an essential, but not sufficient condition for the stimulated emission appearance in strongly confined systems. The absence of negative DT-signal for the hh-e exciton's transitions for colloidal solutions with lower concentration of nanoplatelets can be explained by insufficient pump intensities.

The amplitudes of the DT-signals increase with the growth of pump

intensity. For the solution with low-concentration of nanoplatelets (sample CdSe/CdS15) the saturation of absorption takes place for the both exciton's transitions (see Fig. 2d); the measured saturation intensities are about $I_s \approx 0\ 0.6\ MW/cm^2$ and $I_s \approx 1.1 MW/cm^2$ for the hh-e and lh-e exciton's transitions, correspondingly. For the solutions with moderate- and high-concentrations of nanoplatelets (samples CdSe/CdS19 and CdSe/CdS26) saturation of absorption was found only for the lh-e exciton's transitions (see black squares in Fig. 2e and f); the measured saturation intensities are about $I_s \approx 1\ 0.2\ MW/cm^2$ and $I_s \approx 1.1 MW/cm^2$, correspondingly. The absence of absorption saturation for hh-e exciton's transitions in the solution with high-concentration of nanoplatelets (sample CdSe/CdS26) can be explained by the emergence of optical gain processes. For CdSe/CdS26 nanoplatelets solution, at the wavelength of hh-e exciton's transitions (see red dots in Fig. 2f) the DT-amplitude reveals well pronounced switching from linear growth to the fast decreasing at pump intensities higher than $1 MW/cm^2$. This indicates the presence of a well pronounced crossover from the absorption regime to the optical gain regime. The intermediate situation of linear growth of DT-amplitude corresponding to the hh-e exciton's transitions was found for the solution with moderate-concentration of nanoplatelets (see. Fig. 2e). Similar behavior of DT-amplitude corresponding to the lh-e exciton's transitions for all the concentrations of colloidal nanoplatelets reflects the fact that lh excitons play a role of a reservoir for the hh excitons due to the energy transfer processes [34].

Conclusion

The experimental investigations of the colloidal heterostructured CdSe/CdS nanoplatelets transient absorption in the regime of one-photon stationary excitation of excitons by high-intensity nanosecond laser pulses are discussed in details. The dependence of exciton's transitions behavior on nanoplatelets concentration in colloidal solution and pump intensities was studied for the first time. The revealed nonlinear transmission changes of the nanoplatelets solutions with different optical density were explained by the presence of phase space filling effect, energy exchange between exciton states, re-emission processes and exciton–exciton interaction. The possibility for the existence of the optical gain in colloidal solutions of nanoplatelets was experimentally demonstrated. We believe that obtained results provide the insights on solution-dispersed nanoplatelets utilization for lasing application.

CRediT authorship contribution statement

Alexander M. Smirnov: Investigation, Conceptualization, Writing – review & editing. **Anastasia D. Golinskaya:** Investigation, Writing – original draft. **Vladimir N. Mantsevich:** Conceptualization, Writing – review & editing. **Maria V. Kozlova:** Investigation. **Kseniia V. Ezhova:** Investigation. **Bedil M. Saidzhonov:** Investigation. **Roman B. Vasiliev:** Conceptualization. **Vladimir S. Dneprovskii:** Supervision, Writing – review & editing.

Declaration of Competing Interest

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

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