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Amplified spontaneous emission in colloidal solutions of twophoton-excited CdSe/CdS nanoplatelets

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Abstract. Two-photon processes in CdSe/CdS nanoplatelets were investigated under high intensity excitation by femtosecond laser radiation (1064 nm, 100kHz). The open-aperture zscan technique and the measurement of photoluminescence spectra were utilized for studying their nonlinear optical properties. As a result, two-photon absorption and amplified spontaneous emission at high intensity were found in these nanoplatelets.

1. Introduction

Semiconductor nanocrystals are promising structures for practical applications as biomarkers and gain media due to their unique optical properties. These structures possess high photostability [1,2], a simple production technology, and their properties can be modified in a wide spectral range by varying their sizes and chemical composition [3-10]. To date, most investigations of lasing and amplified spontaneous emission (ASE) in semiconductor nanocrystals have been carried out with their one-photon excitation by means of radiation of the visible or ultraviolet range [11-15]. However, ultraviolet and visible laser radiation can cause photodestruction, photobleaching and self-diffraction [16-18] in nanostructures themselves or objects into which the nanostructures have been implanted for investigation [19, 20]. One of the possible ways to avoid this problem is multiphoton excitation of nanostructures. In this case, the laser radiation is not absorbed in the tissues, has a higher level of tissue penetration and lower Rayleigh scattering [19, 20]. These features improve the sensitivity and resolution at the molecular, cellular level [21] and provide more efficient application of these structures in bio-imaging.

To observe stimulated emission (SE) or ASE in semiconductor nanocrystals, their build-up time has to be shorter than the time of non-radiative Auger recombination of the excited states [21]. The main shortcoming that prevents ASE and lasing in many semiconductor nanocrystals is the high rate of nonradiative Auger recombination of multiexcitons, which suppresses the inverse population and, subsequently, optical amplification [22]. Also, multiphoton excited nanostructures should have a high multiphoton absorption cross section for efficient generation of SE or ASE.

In the recent years, CdSe nanoplatelets (NPLs) or quantum wells have attracted much attention from researchers. First of all, CdSe NPLs are interesting due to the large cross section of two-photon absorption up to 10^7 GM (where 1 GM = 1 Göppert-Mayer = 10^{-50} cm⁴ s photon⁻¹) [23] and the strongly suppressed rate of Auger recombination of excitons in comparison with other semiconductor structures [15, 24, 25]. Exciton dynamics through exciton-exciton [26-28] and exciton-phonon [29] interactions,

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and the second harmonic generation [30] were revealed and studied in a colloidal solution of CdSe/CdS NPLs. Thus, CdSe NPLs are excellent candidates for lasing and ASE generation under multiphoton laser excitation. Up to now, only a few works [12, 21, 31] have investigated lasing and ASE in multiphoton excited nanostructures.

In this work, we studied two-photon light (1lh-1e) and heavy (1hh-1e) exciton excitation in CdSe/CdS NPLs by femtosecond laser radiation. The sample under investigation was synthesized by colloidal method. We have measured the dependences of its transmission on the intensity of incident laser radiation using the open-aperture z-scanning technique and its photoluminescence spectra at different pump power. The measured experimental data were investigated, and nonlinear optical processes in NPLs under two-photon excitation were found.

2. Sample synthesis and characterization

The CdSe/CdS NPLs investigated in this work belong to the core-shell nanoheterostructures and were obtained by applying 3.5 monolayer-thick CdSe NPLs as a core material. The CdSe NPLs were grown according to the procedure described in reference [32]. Shortly, 0.5 mmol of Cd (CH₃COO)₂·2H₂O, 0.2 mmol of oleic acid (OA) and 10 mL of octadecene (ODE) were loaded into a reaction flask. The mixture was degassed at 170 °C under argon flow for 30 min. Then, the temperature was raised to 210 °C, and a mixture of 100 μ L 1M trioctylphosphine selenide and 350 μ L of ODE was injected into the flask. The reaction was continued for 40 min at 210 °C. After that, 0.5 mL of OA was injected into the reaction flask and the mixture was cooled down to room temperature under a water bath. As-obtained NPLs were washed with acetone and redispersed in 6 mL of hexane. Finally, two monolayers of CdS shell were sequentially grown onto the CdSe NPLs following the procedure described in reference [33]. Linear absorption spectrum of the synthesized sample is presented in figure 1. The spectrum has three peaks at 467 nm (2.66 eV), 536 nm (2.31 eV) and 578 nm (2.14 eV), which correspond to the exciton transition from the spin-orbital to the conduction sub-band (1so-1e), from the light hole sub-band to the conduction sub-band (1lh-1e) and from the heavy hole sub-band to the conduction sub-band (1hh-1e), respectively. Three distinct exciton peaks indicate a high quality of the sample (high monodispersity in thickness and a small number of defects in NPLs).



Figure 1. Linear absorption spectrum of a colloidal solution of CdSe/CdS NPLs in a 1-mm cell. The red arrows indicate the wavelength of two-photon laser excitation.

The two-photon absorption of CdSe/CdS NPLs was studied by laser spectroscopy techniques such as an open-aperture *z*-scan and measurements of photoluminescence spectra. The first technique was performed as follows (figure 2): an OptoSystems FL-300 fiber laser was used as a radiation source with a pulse duration of 320 fs and a pulse repetition rate of 100 kHz. The radiation wavelength was 1064 nm (1.17 eV). So the absorption in CdSe/CdS NPLs was realized by means of two-photon interaction

of laser radiation with the excitons (the red arrows in figure 1). The radiation was focused on the sample using a lens with a focal length of 10 cm. The sample was mounted on a mechanical linear translator and moved along the optical axis of the lens around its focus (*z*-axis in figure 2). The power of the incident and transmitted laser radiation was measured by two power meters.



Figure 2. Scheme of the open-aperture z-scan setup: 1 - Optosystems FL-300 femtosecond laser; 2 - half-wave plate; 3 - Glan–Taylor prism; 4 - lens (f = 10 cm); 5 - colloidal solution of CdSe/CdS NPLs in a 1 mm cell; 6 – power meters' sensors; 7 – power meters' consoles.

The scheme for measuring two-photon photoluminescence is presented in figure 3. The laser was utilized in the same mode as in the previous experiment. The pulses intensity of the femtosecond laser was varied in the range from 53 to 315 GW/cm² by means of a half-wave plate and a Glan-Taylor prism in the role of a polarizer. The sample position was fixed at the focus of the lens. Excited photoluminescence radiation of NPLs was collected by a high aperture lens and focused on the waveguide end-face, which was connected to a spectrometer. To prevent appearance of undesirable noise related to the presence of high intensity laser radiation in the spectrometer, an IR-filter was used before the spectrometer waveguide.



Figure 3. Scheme of the experimental setup for measuring photoluminescence of nanoplatelets: 1 - Optosystems FL-300 femtosecond laser; 2 - half-wave plate; 3 - Glan–Taylor prism; 4 - lens (f = 10 cm); 5 - colloidal solution of CdSe/CdS NPLs in a 1 mm cell; 6 - high aperture lens (f = 5 cm); 7 - IR-filter; 8 - fiber waveguide; 9 - Thorlabs CCS100/M spectrometer.

3. Results and discussion

The result of an open-aperture *z*-scan of CdSe/CdS NPLs is presented in figure 4 for different excitation intensities. A decrease in the normalized transmission at about z = 0 mm (figure 4(a), (b)) is explained by the process of two-photon absorption in NPLs. The dependence was approximated by the law for *z*-scan measurements [34]:

$$T_{open}(z) = \sum_{n=0}^{\infty} \frac{(-\beta I_0 L)^n}{(n+1)^{3/2} (1+x^2)^n},$$
(1)

where β is the two-photon absorption coefficient, I_0 is the intensity in focus of the lens, L is the sample length, $x = \frac{z}{z_0}$, where z_0 is the diffraction length of a Gaussian beam. The deviation of experimental data from the fitting curve in the positive *z*-area can be explained by Tyndall scattering of incident radiation in a colloidal solution.



Figure 4. Dependence of the normalized transmission of a colloidal solution of CdSe/CdS NPLs in a 1mm cell on the detuning of the sample from the focus of the lens. (a) $I_{\text{focus}}=72.8 \text{ GW/cm}^2$, (b) $I_{\text{focus}}=78.4 \text{ GW/cm}^2$, (c) $I_{\text{focus}}=245.6 \text{ GW/cm}^2$. Red curve: open-aperture z-scan calculation; green curve: closed aperture; blue curve: simultaneous action of open and closed apertures.

The transmission curve presented in figure 4(c) was measured at a higher intensity characterized by a maximum near the focus and an asymmetric shape. The asymmetric behavior can be explained as follows. On the one hand, the z-scan dependence was measured using a scheme of an open-aperture z-scan, as in previous experiments, which makes it possible to measure nonlinear changes in absorption. However, the approximation function according to expression (1) (red curve in figure 4(c)) did not match the experimental data. On the other hand, self-defocusing of the laser beam that passed through the sample occurred at high intensity, and a part of the laser radiation passed by the power meter sensor, which was placed behind the sample. This case is similar to the measurements of the closed-aperture z-scan technique. A diaphragm placed between the sample and the power meter sensor was used for closed-aperture z-scan measurements. This technique makes it possible to measure nonlinear changes in the refractive index and is described by expression (2) [34]:

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$$T_{closed} = 1 + \frac{4x(\Delta\Phi)}{(1+x^2)(9+x^2)'}$$
(2)

where $\langle \Delta \Phi \rangle$ is the on-axis phase shift at the focus, $x = \frac{z}{z_0}$.

In contrast to the closed-aperture *z*-scan, in our situation the limited aperture of the power meter sensor played the role of a diaphragm for the transmitted laser radiation under high-intensity excitation. The limited aperture *z*-scan is actually a special case of the closed one and should be described by the same expression as the closed aperture. The dependence of the limited (closed) aperture *z*-scan was plotted in figure 4(c) by the green curve, which did not match the experimental data as well. Thus, the experimental result can be explained by the simultaneous action of the peculiarities of open and closed (limited) aperture *z*-scan (nonlinear change in absorption and refraction) and was approximated by multiplication of the functions of both *z*-scans described by formula (1) and expression (2). The resulting curve for open- and closed-aperture *z*-scans was plotted in figure 4(c). This curve approximates well the wings of the experimental dependence and its minimum of transmission shifts relative to z = 0 to the positive *z* values. However, in the range of the maximum intensity, the resulting curve lies lower than the experimentally measured values. It was assumed that the deviation of the experimentally measured values at the maximum intensity from the resulting curve is associated with ASE at 596 nm. The plateau around the focus in figure 4(b) can be explained in the same way.

To validate the presence of ASE, the photoluminescence spectra of nanostructures were measured (figure 5(a)). A broad peak with a maximum at a wavelength of about 596 nm corresponds to the twophoton excited photoluminescence of the colloidal solution of CdSe/2CdS NPLs. The dependence of the photoluminescence intensity on the excitation intensity plotted from these spectra is shown in figure 5(b). At low intensities up to 150 GW/cm², a quadratic dependence (red line in figure 5(b)) was revealed, which can be explained by two-photon absorption in NPLs. At a higher intensity in range from 150 to 290 GW/cm², this dependence becomes linear (blue line in figure 5(b)). This behavior of the experimental data can be associated with the appearance of ASE in the sample under investigation. At intensities above 290 GW/cm², the experimental points are lower than the linear fitting curve. It can be associated with the increasing influence of AUG recombination and thermal degradation of NPLs under high excitation. Thus, the generation of ASE in a colloidal solution of CdSe/2CdS NPLs at a high excitation intensity was confirmed.



Figure 5. (a) Photoluminescence spectra of the CdSe/CdS NPLs in a colloidal solution under the femtosecond pump at a wavelength of 1064 nm. The pulse intensity was varied in the range from 53 GW/cm^2 (purple line) to 315 GW/cm^2 (dark red line). (b) The photoluminescence intensity dependence on the excitation intensity in a colloidal solution of CdSe/CdS NPLs.

4. Conclusions

The nonlinear optical processes were investigated in a colloidal solution of two-photon excited CdSe/CdS NPLs. Two-photon absorption was found in the sample. The peculiarities of the openaperture z-scan dependence at high intensity have been revealed and explained. The generation of ASE has been discovered in the studied NPLs by the open-aperture z-scan technique and confirmed by investigating the measured photoluminescence spectra of nanocrystals.

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