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EXCITONS IN NANOSTRUCTURES

Resonant and Nonresonant Nonlinear Absorption in Colloidal Core/Shell Semiconductor Nanoplatelets[1]

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Abstract—Nonlinear absorption of colloidal solution of core/shell CdSe/CdS nanoplatelets (NPLs) in the case of resonant and nonresonant stationary excitation of the electron/light-hole and electron/heavy-hole exciton transitions was investigated. We have revealed the induced bleaching simultaneously of both exciton transitions. The peculiarities of the nonlinear change in absorption were associated with saturation of exciton transitions absorption due to phase space filling, energy up- and down-conversion mechanisms.

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1. INTRODUCTION

Colloidal solutions of semiconductor nanoparticles are believed to be the promising materials for many applications owing to its unique physical properties that depend chiefly on its size, shape, composition and crystal structure. Colloidal nanocrystals with one-dimension confinement and thickness controlled at the atomic level are called colloidal quantum wells, also more commonly known as nanoplatelets (NPLs). NPLs are good candidates for the analysis of correlation effects and non-stationary processes which were previously widely studied in quantum dots systems [1–6]. NPLs demonstrate superior properties to the other colloidal nanocrystals, including thickness-depend absorption and emission spectra, extremely narrow emission bandwith (<11 nm), small Stokes shift (<10 meV), short radiative lifetime (up to 1 ns at room temperature), enhanced binding energy (owing to the lower dielectric constant $\varepsilon \sim 2$ of surrounding media) and hence increased oscillator strength [7–11].

[1] The article is published in the original.

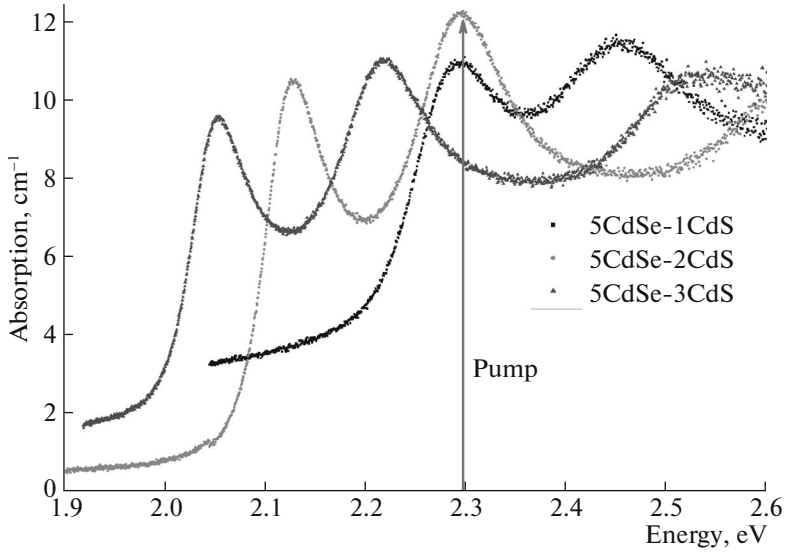

Fig. 1. Absorption spectra of three samples CdSe/CdS NPLs. The arrow corresponds to the second laser harmonic energy.

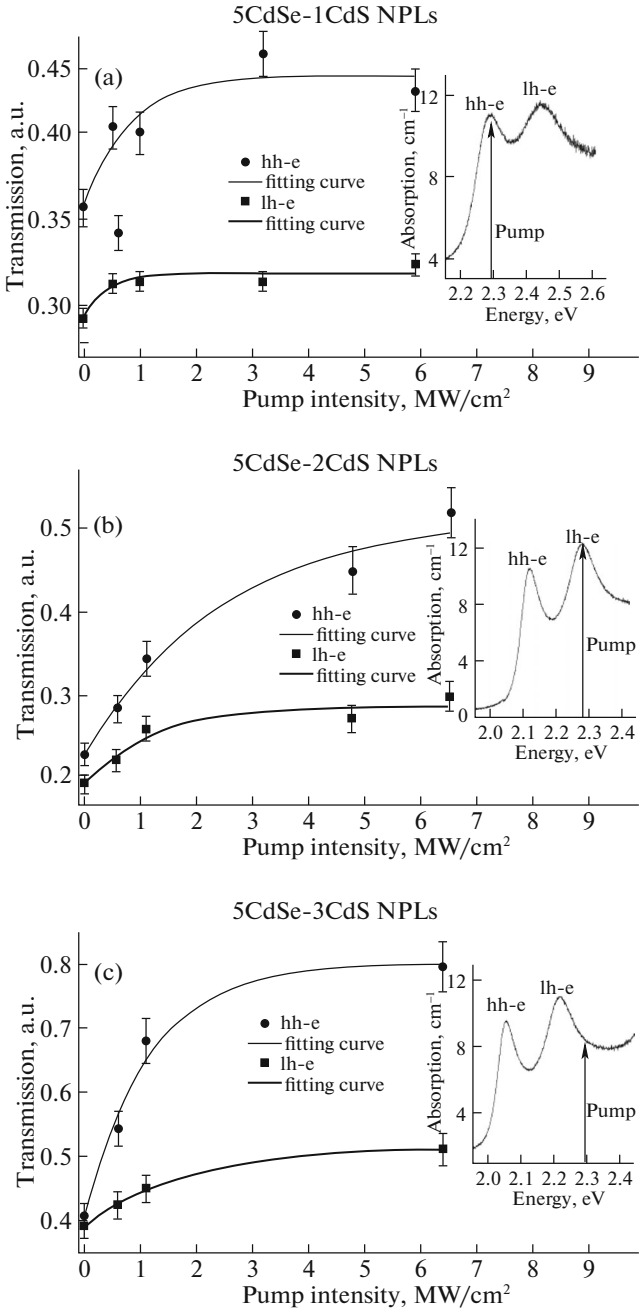

Fig. 2. Nonlinear transmission of three colloidal CdSe/CdS NPLs samples at the wavelength of electron/light-hole transition (black squares) and electron/heavy-hole transition (circles) in the dependence of pump intensity. Insets show an excitation condition.

Typical absorption spectra of CdSe/CdS NPLs exhibit band-edge absorption and two well-resolved exciton transitions. All these properties make the NPLs highly promising for applying in optoelectronic devices, including light emitter, lasers, photodetectors and solar cells.

In this work the nature of nonlinear absorption effect occurring in colloidal core/shell CdSe/CdS NPLs in the case of resonant and nonresonant stationary excitation of the electron/light-hole and electron/heavy-hole exciton transitions has been studied. Comprehensive understanding of nonlinear optical processes fundamental basic occurring in colloidal CdSe/CdS NPLs, let us use its advantages for optical gain and optical limiting applications.

2. EXPERIMENTAL

Three samples of core/shell CdSe/CdS NPLs were studied. Five monolayer CdSe core of NPLs have one, two or three monolayer CdS shell (correspondently, 5CdSe-1CdS, 5CdSe-2CdS, 5CdSe-3CdS). The synthesis of CdSe/CdS heterostructures was carried out by the method [12] of low-temperature layer-by-layer deposition of shell material [9]. The measured absorption spectra of the samples are shown in Fig. 1. Each absorption curve demonstrates two well-resolved exciton maxima that correspond to the electron/heave-hole exciton transition (low energy) and to the electron/light-hole exciton transition (high energy). Decrease of the confinement with shell thickness increasing results in significant red shift of absorption maxima. All measurements were carried out at room temperature.

The pump and probe technique was utilized for investigation of nonlinear absorption effects in colloidal solutions of NPLs. The samples were excited by the second harmonic of Nd^{3+}:$YAlO^3$ laser ($E = 2.3$ eV, the pulse duration is ~10 ns) and probed by broadband photoluminescence of specially chosen coumarin-7 dye excited by the third harmonic of the same laser ($E = 3.4$ eV, the pulse duration is ~9 ns) [13, 14].

3. RESULTS AND DISCUSSION

Nonlinear transmission at the wavelength of exciton transitions in dependence of pump intensity was investigated. It was found that induced bleaching of electron/light-hole and electron/heavy-hole transitions occur simultaneously. The results are presented in Fig. 2.

It was found that as in case of resonant and nonresonant excitation regime the electron/heavy-hole excitons transition bleached to a much greater than electron/light-hole exciton transition due to energy down-conversion. Energy up-conversion from electron/heave-hole exciton to electron/light-hole exciton was revealed in the case of the resonant electron/heave-hole exciton transition in colloidal NPLs with 1 monolayer shell (Inset in Fig. 2a) which led to bleaching of nonresonant high energy electron/light-hole exciton (Fig. 2a). In the case of the resonant excitation of electron/light-hole transition in colloidal NPLs with 2 monolayers shell (Inset in Fig. 2b) and nonresonant excitation of short-wavelength edge of electron/light-hole transition in colloidal NPLs with 3 monolayers shell (Inset in Fig. 2c) both component

of the absorption doublet bleached under the action of high-intensity laser radiation due to phase space filling and energy down-conversion mechanism (Figs. 2b, 2c). There was measured saturation intensity of electron/light-hole and electron/heave-hole exciton transitions in colloidal CdSe/CdS NPLs about 1 MW/cm^2 and a modulation depth of 3–10% for electron/light-hole exciton transition, 8–40% for electron/heave-hole exciton transition.

4. CONCLUSIONS

We have investigated the nonlinear change of the absorption in colloidal solution of CdSe/CdS NPLs at the wavelength of electron/light-hole and electron/heave-hole exciton transitions in the case of the stationary resonant and nonresonant laser excitation. The measured saturation of exciton absorption was explained by phase space filling. Simultaneously bleaching of both exciton transitions was explained by the energy transfer up-conversion and down-conversion mechanisms.

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