Impact of shell material on the nonlinear properties of colloidal CdSe nanoplatelets

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Abstract. The nonlinear change in the absorption of colloidal CdSe nanoplatelets capped with a CdS-shell and a ZnS-shell was investigated in the case of the steady-state excitation regime. It was revealed that the nonlinear optical response of planar heterostructured nanocrystals is strongly influenced by the crystal structure of the core and shell material.

1. Introduction
Colloidal nanoplatelets are atomically flat nanocrystals with lateral sizes of about tens of nanometers. These planar nanostructures have the electronic properties of two-dimensional (2D) quantum wells and possess thickness-tunable absorption and emission spectra [1-3]. Optical properties of ensembles of semiconductor nanoplatelets are characterized by a narrow emission line at room temperature (full-width at half-maximum as small as 7-10 nm), a giant oscillator strength of optical transitions together with a short exciton decay time. These properties make this new class of nanocrystals a promising candidate for application in optoelectronic devices such as LEDs, lasers, polarized emitters, light emitting diodes and solar cells [4-8]. The growth of a shell on such a quasi 2D system can greatly improve surface passivation, photoluminescence quantum efficiency, and enhance the photostability [9-10]. Core/shell heterostructured nanoplatelets are remarkable in the sense that their optical properties can be additionally tuned through control of the spatial distribution of the electronic wave function between the core and shell regions. There a number of experimental and theoretical studies of the stationary excitation of excitons in quasi 2D structures. In the case of resonant excitation of excitons, the bleaching of both exciton transitions was revealed and explained by the effect of exciton phase space filling, energy exchange processes between excitonic states and exciton-exciton interaction [11, 12]. In the case of non-resonant excitation of excitons, the bleaching of heavy excitons was revealed and explained by the effect of partial filling of the exciton phase space owing to the interaction with longitudinal optical phonons, while the bleaching of light excitons was not detected [13]. It is known that the shell thickness and composition have a dramatic impact on the dynamics of exciton decay, exciton-phonon interaction and the photoluminescence decay kinetics [14, 15].
colloidal core/shell nanoplatelets, while the effect of the shell structure on the nonlinear properties of nanoplatelets is still unclear.

In this paper, we for the first time investigated the nonlinear optical response of CdSe nanoplatelets, depending on the shell materials. The role of the lattice mismatch between the shell and the core in a nonlinear decrease in absorption due to a significant difference in the rate of non-radiation decay is revealed.

2. Experimental details
CdSe Nanoplatelets with an emission wavelength of 466 nm were obtained using the method reported in [1]. Then, the CdS (ZnS) shell material was grown on the core nanoplatelets using a technique of colloidal atomic layer deposition, as described in detail in [16]. Transmission electron microscopy images (TEM) of the samples are shown in figure 1.

![Figure 1](image1.png)

**Figure 1.** TEM images of (a) CdSe/1CdS and (b) CdSe/3ZnS heterostructured nanoplatelets.

The nonlinear optical response of studied core/shell nanoplatelets was measured by using the pump-probe technique described in [17]. Pumping was performed by the second harmonic of a Q-switched Nd³⁺:YAlO₃ laser (λ = 540 nm, pulse duration of about 10 ns). For both samples, the photon energy of the second harmonic of laser radiation coincides with the electron/heavy-hole exciton transition. Probing was carried out by using the broadband photoluminescence radiation of the Coumarin-7 dye excited by the third harmonic (λ = 360 nm) of the laser. Durations of the pumping pulses (~ 10 ns) exceeded the recombination time of excitons in nanoplatelets. Thus, the quasi-stationary resonant excitation regime was realized. The intensity of the pump radiation was 8.6 MW/cm². The spectra were measured and recorded on a PIXIS 256 CCD camera combined with a SpectraPro 2300i polychromator. All the measurements were carried out at room temperature.

3. Results and discussion
The measured linear and nonlinear absorption spectra of colloidal CdSe/1CdS and CdSe/3ZnS nanoplatelets are presented in figure 2.

The linear absorption spectra exhibit two well-resolved excitonic peaks. The high-energy (low-energy) peak corresponds to excitation from a light-hole (heavy-hole) valence band state to a conduction band state (LH-e and HH-e, respectively). At the resonant excitation of heavy-hole excitons, the decrease in absorption was observed in the vicinity of HH-e and LH-e exciton transitions simultaneously. This phenomenon was explained by the effect of exciton phase space filling, energy up- and down-conversion mechanisms and interaction between excitons in core/shell nanoplatelets [11, 12]. It was found that a decrease in absorption at the excitation wavelength is significantly larger for the CdSe/1CdS sample compared to the CdSe/3ZnS sample. The insets of figures 2(a) and 2(b) show the differential absorption spectra DA:

\[
DA = \frac{(A_0(\lambda) - A_e(\lambda))}{A_0(\lambda)},
\]
Figure 2. Linear (black line) and nonlinear (red line) absorption spectra of the colloidal solutions of core/shell (a) CdSe/1CdS and (b) CdSe/3ZnS nanoplatelets. The insets show the differential absorption spectra of corresponding samples (blue line).

where $A(I, \lambda)$ and $A_0(\lambda)$ are the absorption spectra of the excited and non-excited samples. A relatively small optical response of CdSe nanoplatelets capped with a ZnS-shell is due to lots of crystal defects at the heterostructure boundary. The folding effect of CdSe/3ZnS nanoplatelets was observed (figure 1(b)) and explained due to a shell-induced contractive strain [16]. The lattice mismatch between the CdSe-core (sphalerite $a = 6.077$ Å) and the ZnS-shell (sphalerite, $a = 5.345$ Å) is larger compared to the lattice mismatch between the CdSe-core and the CdS-shell (sphalerite, $a = 5.81$ Å). Numerous induced defects in CdSe/3ZnS lead to an increase in the rate of non-radiative Auger recombination of excitons and a reduction in the nonlinear change of absorption.

4. Conclusion
In summary, the nonlinear absorption spectra of colloidal CdSe/1CdS and CdSe/3ZnS nanoplatelets were studied in the case of excitation of heavy hole excitons by high-power nanosecond laser pulses. It was shown that the nonlinear optical response of colloidal core/shell planar nanocrystals substantially depends on the crystal structure of the shell and core materials.

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