Dependence of the nonlinear optical response of CdSe nanoscrolls on coating with oleic or acetic acid

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Abstract. The photoluminescence and nonlinear transmission of atomically thin population of colloidal CdSe rolled-up nanosheets were investigated at the one-photon stationary excitations of excitons by the third harmonic of Nd³⁺:YAP laser pulses. It was revealed that the nonlinear optical response of the nanoscrolls is strongly influenced by multiwalled rolled-up structure. The broadening of exciton band and the red shift of the photoluminescence were observed and explained by coupling effect within the folded scroll-layers.

1. Introduction

Atomically flat nanoplatelets with precise thickness control have attracted a great deal of attention because of their remarkable optical and electronic properties, originating from strong spatial confinement of excitons in one direction and their morphological perfection [1]. Among various types of two-dimensional colloidal nanocrystals, the semiconductor CdSe nanoparticles with complicated shape, including nanoribbons, nanobelts and nanoscrolls, are promising materials for applications in polarization-enabled devices due to their strong optical activity [2].

In this work photoluminescence (PL) properties and nonlinear transmission of the 2.5-monolayer-thick CdSe nanoscrolls covered with oleic and acetic acid were investigated at the one-photon stationary excitation regime. Ligand exchange of native oleic acid molecules with shorter length acetic acid ones provides the reduced distance between layers in folded nanoscrolls.

2. Experimental details

2.1. Samples.

The synthesis of 2.5-monolayer-thick CdSe nanoscrolls followed the article [3]. Briefly, synthesis of nanoscrolls was carried out by the colloidal method in the octadecene – cadmium acetate – oleic acid system. After degassing (170-190°C) a mixture of 0.13 g cadmium acetate dihydrate and 10 ml octadecene, the injection temperature (120°C) was set, 200 µl of selenium precursor (1 M solution of selenium in trioctylphosphine) was injected, after which the temperature gradually increased to the growth temperature (160°C) and maintained constant for 4 hours. At the end of the synthesis, 1 ml of oleic acid was added as a stabilizer. The resulting nanoparticles covered with oleic acid (CdSe-OA sample) were separated by centrifugation with an acetone precipitator and dissolved in hexane. To obtain a the second sample, a thermodynamically advantageous substitution of long unsaturated oleic acid for...
short acetic acid was performed at room temperature in hexane. In the following, the scrolls covered with oleic acid and acetic acid are denoted as CdSe-OA and CdSe-AA, respectively. The covering of nanoparticles with acids are required for passivation surface.

2.2. Experimental setup
The optical response of the samples was investigated with modification of pump and probe technique described in [4]. The difference is that the probing of transmission changing was realized by organic dye radiation. Briefly, the pump was realised by the third harmonic of Nd\textsuperscript{3+}:YAP laser pulses (λ=360 nm, τ=9 ns); the pump power varied from 130 kW/cm\textsuperscript{2} to 2.1 MW/cm\textsuperscript{2} by optical neutral filters. The radiation of BBQ organic dye (C\textsubscript{48}H\textsubscript{66}O\textsubscript{2}, 4,4''-Bis-(2-butyloctyloxy)-p-quaterphenyl) was used as probe signal; the wavelength of the BBQ dye PL spectrum coincides with the absorption band of heavy hole-electron (hh-e) exciton transition of the samples. All measurements were performed at room temperature.

3. Results and discussions
The PL spectra of the CdSe-OA and CdSe-AA scrolls for different pump intensities are presented in Figure 1a and Figure 1b, respectively.

![Figure 1](image_url)

**Figure 1.** The PL spectra of the CdSe-OA (a) and CdSe-AA (b) scrolls for different pump intensities. Pump intensities varied from 0.1 W/cm\textsuperscript{2} to 2.1 MW/cm\textsuperscript{2}.

For both samples PL spectra demonstrate a narrow luminescence peak (around 400-410 nm) associated with the lowest excitonic transition together with wide longwavelength luminescence band (around 520 nm) caused by the radiative carrier recombination through trap-related states. The intensities of the PL maxima of both emission bands increase with the growth of the pump intensity. Under the same excitation conditions, the excitonic PL intensities of both samples are approximately equal but trap-assisted PL intensity in CdSe-AA sample is significantly higher than trap-assisted PL intensity in CdSe-OA. Numerous induced defects in CdSe-AA sample are due to the folding effect caused a strong mechanical strain [3, 5]. For both samples the long wavelength Stokes shift of the exciton PL was found with the growth of excitation intensity. Its value increases from 8 nm (70 meV) for the lowest excitation intensity to 12 nm (100 meV) for the highest excitation intensity and from 14 nm (110 meV) to 20 nm (150 meV) for CdSe-OA and CdSe-AA, respectively. The revealed red shift of the PL spectra with increasing pump power can be the evidence of the formation of excited dimers and their radiative recombination at room temperature [6].

The measured linear and nonlinear transmission spectra of the CdSe-OA and CdSe-AA scrolls at the highest pump intensity are presented in Figure 2a and Figure 2b, respectively.
Figure 2. The linear (black line) and nonlinear (red line) transmission spectra of the CdSe-OA (a) and CdSe-AA (b) scrolls. The insets show the experimental (grey line) and smoothed (blue line) differential transmission spectra of the corresponding samples.

The broadening and slight red shift (3 nm) of exciton band was found for CdSe-AA sample, compared to the CdSe-OA one. The observed shift and broadening of CdSe-AA scrolls absorption spectrum is explained by the folding effect caused a strain appearance under acetic acid attachment [3, 5]. The modification of the exciton bands can be also assigned to the coupling effects within the rolled-up nanosheets as in quantum-dot dimer molecules due to the decreasing of interwall spacing [7]. The quantum coupling can lead to modifying of energy structure and the formation of minibands, promoting the red shift of absorption spectrum. The differential transmission (DT) spectra were measured to investigate the nonlinear properties of the scrolls (insets in Figure 2a and Figure 2b):

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DT = \frac{T(\lambda, I) - T_0(\lambda)}{T_0(\lambda)},
\]

where \(T_0(\lambda)\) and \(T(\lambda, I)\) – the linear and nonlinear transmission spectrum, respectively. For both samples the significant bleaching of hh-e exciton transition was observed as a result of the phase space filling effect, energy transfer between excitons [4, 8-10] and interaction with phonons [11]. The negative DT-values were observed in in the wavelength region about 410 nm that can be caused by the broadening of absorption peaks due to exciton-exciton interaction under the action of high-intensity laser radiation [8,10].

4. Conclusion
The nonlinear optical response of oleic acid and acetic acid capped CdSe nanoscrolls were investigated by means of pump and probe technique. The role of interlayer carrier-interaction in the PL properties and transient absorption of colloidal CdSe scrolls was revealed experimentally by the observed broadening of absorption spectrum and red-shifting of PL spectra with the growth of pump intensity.

Acknowledgment
This work was supported by President grant for young scientists MD-781.2021.1.2 and Russian Foundation for Basic Research (20-32-70001).

References
[1] Itthuria S, Tessier M, Mahler B, Lobo R, Dubertret B, Efros A 2011 Nat. Mat. 10 936
[2] Ma W, Xu L, de Moura A, Wu X, Kuang H, Xu C, Kotov N 2017 Chem. Rev. 117 8041
[3] Kurtina D, Garshev A, Vasil’eva I, Shubin V, Gaskov A, Vasiliev R 2019 Chem. Mater. 31 9652.
[4] Smirnov A, Golinskaya A, Kozlova M, Zharkova E, Saidzhonov B, Vasiliev R, Dneprovskii V 2020 Semicond. 54 1907
[5] Vasiliev R, Sokolikova M, Vitukhnovskii A, Ambrozevich S, Selyukov A, Lebedev V 2015 Quantum Electron. 45 853
[6] Diroll B, Cho W, Coropceanu I, Harvey S, Brumberg A, Holtgrewe N., Crooker A, Wasielewski M, Prakapenka V, Talapin D, Schaller R 2018 Nano Lett. 18 6948
[7] Cui J, Panfil, Koley Y, Shamalia S, Waiskopf D, Remennik S, Popov I, Oded M, Banin U 2019 Nat. Comm. 10 1
[8] Smirnov A, Golinskaya A, Saidzhonov B, Vasiliev R, Mantsevich V, Dneprovskii V 2021 J. Lum. 229 117682
[9] Smirnov A, Mantsevich V, Smirnov D, Golinskaya A, Kozlova M, Saidzhonov B, Dneprovskii V, Vasiliev R 2019 Sol. St. Comm. 299 113651
[10] Smirnov A, Golinskaya A, Zharkova E, Kozlova M, Saidzhonov B, Vasil’ev R, Dneprovskii V 2019 JETP Lett. 109 454
[11] Smirnov A, Golinskaya A, Saidzhonov B, Vasiliev R, Mantsevich V, Dneprovskii V 2019 JETP Lett. 109 372