Nonlinear optical properties of hybridized CdS/ZnS-PVP sols

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Abstract. Hybrid composites of CdS-core ZnS-shell nanoparticles embedded in polyvinylpyrrolidone (PVP) matrixes have been prepared and characterized. Cadmium sulfide (CdS) nanocrystals were grown in water-propanol-2 solutions containing high-molecular (Ms=1300000) polyvinylpyrrolidone (PVP) at room temperature using cadmium nitrate and sodium sulfide as the cadmium and sulfur sources, respectively. The CdS/ZnS-PVP suspensions have promising optical properties for nanocomposite films based on. Nonlinear optical properties of diluted CdS/ZnS sols were studied at 532 nm and 5 ns laser pulses by using the Z-scan technique. Dependence of the nonlinear-optical coefficients on the CdS weight has been obtained.

1. Introduction
The quantum-sized CdS nanocrystals has an exceptional third-order nonlinear optical properties useful for optical switches or limiting devices [1,2]. The ZnS shell stabilizes the size of quantum dots (QDs) and improves the quantum yield of luminescence [3]. To realize optical devices, the nanoparticles should be integrated into a solid-state matrix, e.g. glass or polymer [4]. The nanocrystals must be homogeneously distributed in the matrix and save stable properties. Polymers are considered a good choice as host materials due to their relatively architectural flexibility, simple fabrication process and low cost [5]. Among all the useful polymeric materials, polyvinylpyrrolidone (PVP) belongs to a neutral charged polymeric dispersant and has outstanding colloidal and complexing properties [6,7]. PVP has been widely used as the protecting agent or stabilizer for synthesizing nanoparticles [8,9] and the matrix for manufacturing the optical devices [10,11]. In this paper we studied nonlinear optical properties of hybridized CdS/ZnS-PVP sols (in situ) by excitation of laser radiation at λ = 532 nm and 5 ns pulse with higher intensity. Nonlinear coefficients of refraction γ (cm²/W) and two photon absorption (TPA) β (cm/W) were extracted from the analysis of the z-scan technique data [12]. The excitation was carried out in the transparency region of QDs and an effective two-photon absorption process was observed. Investigated sols have promising nonlinear properties for switching devices and for creating films based on.

2. Methods
Cadmium sulfide (CdS) nanocrystals were grown in water-propanol-2 solutions containing high-molecular (Ms=1300000) polyvinylpyrrolidone (PVP) at room temperature using cadmium nitrate and sodium sulfide as the cadmium and sulfur sources, respectively. CdS nanocrystals were perfectly stabilized by PVP molecules without the formation of precipitates, the concentration of CdS was about...
The band gap values of semiconductor nanoparticles in liquid solutions and composite coatings were obtained by the analysis of optical spectra by using Tauc’s equation [13]. From these data was calculated the diameter of quantum dots. A field-emission scanning electron microscope was employed to examine the size and distribution of the resultant CdS nanocrystals in the PVP matrix. Z-scan is an effective technique to investigate nonlinear absorption and nonlinear refraction. The experiment was performed by method, described in [10]. Nanoparticles were excited at the wavelength of the second harmonic of YAG:Nd$^{3+}$ laser ($\lambda_{ex} = 532$ nm), $\tau_{pulse} = 5$ ns, $E = 100$ $\mu$J. Gaussian beam focused by a lens with $F = 15$ cm. The cell with the solution ($d = 2$ mm) was moved automatically along the main optical axis passing successively to positions before the focal plane ($-z$) and after it ($+z$). The output energy of the cell was measured by a photometer (OPHIR) in two regimes "closed aperture" and "open aperture", that allowed us to separate the nonlinear refraction from the nonlinear scattering and absorption.

3. Results and discussion
The absorption spectra measurements of sols were carried out on a spectrophotometer Lambda 1050 Perkin Elmer (Figure 1).

Figure 1. The absorption spectra of CdS/ZnS-PVP sols with different CdS mass concentration: 1 – 0.8 mM, 2 – 1.4 mM, 3 – 2.8 mM, 4 – 4.2 mM.

In Figure 1, the main exciton absorption peak of quantum dots near 400-420 nm is clearly visible, which corresponds to the $1S_{1/2}(e)$-$1S_{3/2}(h)$ transition. The energy of the band gap and the diameters of the quantum dots were calculated in accordance with the Tauc’s equation [13]. The diameters of the synthesized quantum dots were about 2-4 nm. On the QDs spectra 3 and 4 (Figure 1) the bands corresponding to the $1P(e)$-$1P_{3/2}(h)$ transition with an energy of about 4.1 eV are also resolved. The synthesized sols showed high stability over time.

The position of the laser wavelength $\lambda_{ex} = 532$ nm corresponds to the transparency region of the investigated sols, but at high intensities we have the increased transitions probability with a doubled
photon energy is 4.6-4.7 eV. Nonlinear absorption, self-focusing and defocusing, generation of the third harmonic, etc. are described by the cubic nonlinear susceptibility tensor $\chi^{(3)}$, it is a complex quantity $\chi^{(3)} = \text{Re}\chi^{(3)} + i\text{Im}\chi^{(3)}$. The $\text{Im}\chi^{(3)}$ is responsible for nonlinear absorption, and the real part describes a nonlinear change in the refractive index $\gamma$ ($\gamma$ is nonlinear refraction index that is due to the bound electrons and is related to the usual nonlinear index $n_2$ through $n_2 = c n_0 \gamma / 40 \pi$ [14]). If we confine ourselves to considering only third-order nonlinearity, then the following relations are satisfied for the coefficients $\gamma$ (cm$^2$/W) and $\beta$ (cm/W):

$$\chi_{im}^{(3)} = \frac{n_0^2 \varepsilon_0 c^2}{\omega} \beta$$

(1),

$$\chi_{Re}^{(3)} = 2n_0^2 \varepsilon_0 c^2 \gamma$$

(2)[12].

Figure 2 shows the experimental dependences of the transmission of laser radiation as a function of the sample $z$ position with respect to the focal plane of the CdS/ZnS-PVP sol with a maximum concentration. The closed aperture-measurements for the sample near the focus plane demonstrates the valley-peak behavior, it characterizes the positive refraction (self-focusing of the radiation). The removal of the aperture showed the contribution of two-photon absorption and scattering.

![Figure 2](image)

**Figure 2.** The Z-scan results of CdS/ZnS-HMW-PVP sol (C=8.4·10$^{-3}$ M): squares represent normalized transmittance for the open aperture; dots are data by the closed aperture $A=0.2$ (with removed open data). The lines are drown for clarity. Parameters of pulse $\lambda_{ex} = 532$ nm, $t=5$ ns, $I = 0.4$ GW/cm$^2$.

The calculated coefficients of two-photon absorption and nonlinear refraction for all available CdS mass concentrations are presented in Table (below). In the case of an open aperture, the relative error was 4.8%, in the case of a closed aperture, 10%. The main contribution to the discrepancy was determined by the spatial instability of the laser beam. Each point in Fig. 4 is obtained by averaging over 5 mono pulses.
Table. TPA and nonlinear refraction coefficients of CdS/ZnS QDs, stabilized by PVP ($I = 0.4 \text{ GW/cm}^2$)

| Concentration CdS (in situ), M | T₀, % | β, cm/GW | γ, cm$^2$/W |
|-------------------------------|-------|----------|-------------|
| 1.7·10$^{-3}$                 | 88.2  | 1.9      | -           |
| 2.8·10$^{-3}$                 | 86.7  | 2.9      | 3·10$^{-14}$|
| 5.6·10$^{-3}$                 | 83.0  | 4.2      | -           |
| 8.4·10$^{-3}$                 | 82.8  | 5.3      | 7·10$^{-14}$|

Taking into account the low excitation energy and the predominance of bound electrons refraction, the positive refraction sign means, that excited states of QDs are connected by two-photon transition with energy close to $E_g$ value. Similar mechanism was confirmed in studies of CdS and other nanoparticles [14,15]. In our opinion, the influence of the molecular environment cannot be ruled out. The positive refraction is described also in [16,17] under the femtosecond laser radiation at wavelengths 750-800 nm, while the $\gamma$ values deviate both towards higher and lower values depending on the environment matrix (see table in [18]).

The two-photon absorption coefficients $\beta$ show a well-marked linear dependence on the CdS QDs concentration (Figure 5) (with accuracy of 98%). It is obvious, because of increasing in absorbing centers per unit irradiated area.

![Figure 3](image)

**Figure 3.** The linear dependence of experimental TPA coefficients $\beta$ (cm/GW) on CdS mass concentration in high-molecular PVP-sol.

We see, that at the highest CdS concentration, TPA coefficient $\beta$ of nanoparticles is comparable with that for bulk CdS 5.4 cm/GW [19]. However, the molar concentration $C_\mu$ of the bulk material is 10$^4$ times higher (for bulk CdS $C_\mu = \rho/M = 33.4$ M), which indicates an improvement in the nonlinear properties of nanoparticles compared to a bulk semiconductor. Performed experiments with third detector showed the presence of nonlinear scattering. The quantitative contribution to the transmittance decrease of it in relation to TPA in investigated sols remains discussion.
4. Conclusion

Synthesized highly stable hybridized CdS/ZnS-PVP sols have non-linear absorbing properties exceed considerably the values for the bulk material under the same conditions. Two photon absorption coefficients depend on CdS concentration in direct ratio. The nonlinear refraction mechanism for about 2 nm diameter synthesized quantum dots excited by the 532 nm laser wavelength appeared to be a positive lens. The hybrid CdS/ZnS-PVP sols can be used to create polymer coatings in photoelectronic devises.

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