Photodecomposition of organic/inorganic composite materials based on polyvinylpyrrolidone

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Abstract. The photodecomposition under UV light and powerful laser (\(\lambda = 532\) nm) irradiations of organic/inorganic solutions and composite coatings containing organic diazo dye has been studied. The presence of zinc nitrate significantly changes the behavior of spectral properties evolution at UV irradiation and significantly accelerates the photolysis of organic dye. It was found that prepared composite CSB/Zn(NO\textsubscript{3})\textsubscript{2}/PVP and CSB/PVP coatings demonstrate the high transparency and non-linear optical properties in visible spectral range and can be used as limiters of powerful laser irradiation.

1. Introduction
The organic/inorganic composite materials based on polyvinylpyrrolidone (PVP, Fig.1) are promising for different optical applications. The aim of this work is the study of the photodecomposition under UV light and under powerful laser (\(\lambda = 532\) nm) irradiations of organic/inorganic solutions and composite coatings based on PVP and containing organic diazo dye. The presence of organic dye Chicago Sky Blue (CSB) in the solutions and CSB/Zn(NO\textsubscript{3})\textsubscript{2}/PVP composite coatings allows to estimate photocatalytic properties of these materials. The structure and spectral properties of this dye was described in [1] in detail.
It’s known that the addition of aromatic hydrocarbons into the materials structure can enhance non-linear optical properties of obtained composites [2]. The composite based on PVP demonstrate high non-linear optical properties and transparency in visible spectral range [2,3]. Moreover, the composite coatings may be deposited on the surface of solid material by simple technique (spraying; dipping process). Therefore, PVP-based transparent composite coatings could be considered as promising material for thin temporal non-linear optical limiters.

2. Materials and Methods
The aqueous solutions of Zn(NO\textsubscript{3})\textsubscript{2} (0.11 M), organic diazo dye Chicago Sky Blue (CSB; Sigma-Aldrich, Fig. 2) (8.7 \(10^{-6}\) M) and the solution of PVP (\(M_w=1300000\)) in propanol-2 (1.1\(\cdot\)10\textsuperscript{-3} M) were used as raw materials. The composite CSB/Zn(NO\textsubscript{3})\textsubscript{2}/PVP solutions were prepared by mixing these initial solutions.
The composite CSB/Zn(NO$_3$)$_2$/PVP coatings were prepared on the glasses by the dipping method. The specimens were first put into the solution, then were withdrawn from it and were dried under 50°C for 24 hours. The absorption spectra were measured with Shimadzu UV-3600 spectrophotometer. The UV irradiation was carried out using high pressure Hg lamp (DRT-250 (Russia)). The power density of light irradiation incident on the experimental sample was 0.25 W/cm$^2$.

The non-linear optical measurements were performed using z-scan technique [1]. The source was a frequency doubled Nd:YAG laser with pulse parameters: $\lambda _{ex}$=532 nm, $\tau _{pulse}$=5 ns, $E_{pulse}$= 0.5-2 $10^4$ µJ. Beam with Gaussian profile was focused by the lens with F=15 cm. There are two photometers (OPHIR) was used for energy detecting; the output energy was measured in two regimes "open aperture" and "closed aperture". 2 mm cell was in case of sols. The optical scheme consisted of laser source, beam splitter, filters, expander, lens, automated shift with sample holder, detectors.

![Figure 1. The structure of the PVP](Image)

![Figure 2. The molecular structure of Chicago Sky Blue dye](Image)

3. Experimental results and discussions

3.1. Spectral properties

The absorption spectrum of composite coatings containing CSB dye is shown in Fig.1. The intensive absorption band which is characteristic for this dye is observed in red part of visible spectral range. Fig.1 shows that two maximums are observed in the spectrum of the composite coating. This phenomenon is related to the intermolecular interaction and the formation of the dimers and trimers of CSB molecules [1]. At low dye concentration CSB molecules in solutions and organic polymer are in monomer form, but at the concentration more than ~ $10^{-6}$ M they interact with each other and form the dimers and trimers of dye molecules [1]. These molecular aggregates have the spectral properties slightly differs from monomers and maximum of their absorption band is located at longer wavelengths.

UV irradiation decomposes diazo dye CSB both in aqueous solutions and composite coatings. Fig.3 demonstrates the changes of CSB/Zn(NO$_3$)$_2$/PVP composite coating during UV irradiation. The intensity of CSB absorption band significantly is reduced after UV irradiation. Also, the shape of absorption spectra changes significantly demonstrating photodecomposition of dimers and trimers of CSB molecules.

The kinetics of CSB photodecomposition in the mixed solutions is shown in Fig.4. It was found that CSB photolysis proceeds significantly faster in the pure CSB solution (Fig.4, curve 1) and in the CSB solution with metal nitrate addition (Fig.4, curve 2) than in coating (Fig.4, curve 3). Almost full decomposition of CSB dye in the solution containing zinc nitrate is observed after UV irradiation during 15 min (Fig.4, curve 2). In the composite solution without zinc nitrate the photodecomposition proceeds very slowly. Full decomposition CSB in composite coating isn't observed after UV irradiation during 60 min.
It was found that the presence of zinc nitrate in the coating composition hasn’t influence on the spectral properties of CSB and on the kinetics of dye decomposition.

3.2. Nonlinear transmittance at 532 nm
Synthesized CSB/Zn(NO$_3$)$_2$/PVP and CSB/PVP composite coatings and sols were investigated in two modes of laser action. The sample was placed in the focal plane of the positive lens ($F=+15$ cm). In the first case, the sample was fixed, and input energy was changed by means of calibrated neutral filters. In the second case, vice versa, input energy was fixed and the sample was moved along the optical axis, passing successively before the focal plane positions and after (the z-scan method). The threshold of sensitivity, when nonlinear effects appeared, was about 0.2 GW/cm$^2$ for all samples (Fig. 5).

Investigations of samples resistance showed, that starting from 2 GW/cm$^2$, the optical limiting (nonlinear transmittance reducing) in the case of the CBS/PVP coating and the bleaching effect in the
case of the CSB/Zn(NO$_3$)$_2$/PVP coating occurred irreversibly (Fig. 5). The maximum attenuation rate for the coating without nitrates reached 50 times at the intensity $I=2$ GW/cm$^2$, and its evaporation occurred at intensities of about 5 GW/cm$^2$. A comparison of the coatings of the two compositions in the frequency regime of 10 Hz and at an intensity of 5 GW/cm$^2$ showed that the ratio of the absorbed energies to the breakdown point was 2.5, and CSB/PVP coating is harder (not shown). Consequently, the presence of nitrates negatively affects the resistance to laser radiation, which, as noted above, is associated with the acceleration of the degradation of dye molecules under exposure. Unlike coatings, solutions of similar compositions were only bleaching at the high energies (Fig.5, 3 and 4 measurements), therefore their use as nonlinear optical filters [5] is difficult. We note, that using of synthesized CSB/PVP coatings as laser radiation limiters of nanosecond duration is possible in case of high intensities about 2-5 GW/cm$^2$, including for several seconds at a repetition rate of 10 Hz.

Investigations by z-scan method have shown differences between sols and coatings, between presence of nitrates and absence (Fig. 6).

As can be seen from the spectra on Fig. 3, the synthesized samples absorb radiation with 532 nm wavelength weakly. Consequently, transmission decrease with increasing power density on Fig. 6 at open aperture regime is due to nonlinear scattering primarily. During z-scan measurements, it was observed strong scattering from samples. We found, that nonlinear properties of coatings and sols are similar in many ways. Principled difference appeared in the regime of open aperture. In CSB/Zn(NO$_3$)$_2$/PVP sol the “valley” is more narrow and dip than in CSB/PVP sol. In case of coatings we registered weak bleaching at nitrate presence, in case of sols it was absorbance (Fig.6 (a), (b)). It is explained by the small number of scattering centers in a thin coating layer and additional saturable absorption of dye molecules at nitrates present. Curves 2 on Fig. 6 indicate, that important mechanism changing transmittance trend is nonlinear refraction also. The change of valley to peak in closed aperture regime corresponds to positive refraction. The shape of the transmittance curve is asymmetric for both the coatings (not shown) and the sols, what requires more detailed consideration of mechanisms. In the case of coatings, the z-scan curves measured with a closed aperture are almost identical; they indicated a positive character of refraction and are asymmetric with respect to the focus. Measurements of sols allow us to make a more qualitative assessment of the differences in the mechanisms of nonlinear transmission for the presence of nitrates and absence. From Fig. 6, it can be seen that in a liquid medium, nitrates negatively affect the formation of a positive lens at the focus of exposure. Thus, the presence of nitrates reduces ability to optical limiting. Calculation of the coefficients of nonlinear scattering and refraction is an important task for these coatings and will be carried out in future studies.

![Figure 6. Z-scan measurements of sols: (a) is CSB/PVP; (b) is CSB/Zn(NO$_3$)$_2$/PVP. (I) is open aperture regime of z-scan; (2) is close aperture regime of z-scan (normalized to open). $I_{in, focus}$, $Z=0 = 0.2$ GW/cm$^2$. $T/T_{0}$ is normalized transmittance; $Z$ is distance from focal plane to the sample (the movement was from lens to detector in each case).](image)
4. Conclusions

The presence of zinc nitrate significantly changes the behavior of spectral properties evolution at UV irradiation and significantly accelerates the photolysis of organic dye. It was found that prepared composite CSB/PVP coatings demonstrate the high transparency and non-linear optical properties at the 532 nm wavelength and can be used as limiters of nanosecond laser pulses at intensities of about 2-5 GW/cm², in including within a few seconds with frequency action (10 Hz).

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