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LINEAR AND NONLINEAR OPTICAL CHARACTERIZATIONS OF TiO_2-BASED HYBRIDS AT THE SELF-ACTION OF CW LASER IRRADIATION AND PICOSECOND LASER PULSES

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The impact of the concentration of TiO_2 nanoparticles on the optical and nonlinear optical (NLO) response of TiO_2-based hybrids is studied. The characterization of variations of the optical scattering, photoinduced absorption, and refractive index under the excitation of continuous (CW) and picosecond laser pulses of studied samples is performed. The manifestation of the cooperative effect of nanoparticles at concentrations higher 4.4×10^{20} cm^{-3} of Ti atoms is observed. The effect is accompanied with the enhancement of the efficiency of charge separation processes at the organic-inorganic interface and with the photoinduced Ti^{3+} centers polarizability reduction. The observed results indicate the optimal titanium concentration about 4.4×10^{20} cm^{-3} for the photonics application.

Keywords: nonlinear optical response, self-action effect, cubic nonlinear optical susceptibility, charge separation efficiency.

1. Introduction

The organic-inorganic hybrids are widely recognized as one of the most promising several alternative cost-effective substances for the application to the information storage, optical switching, and photonic devices [1]. The combination of the useful properties of organic matrices with the photoactivity of incorporated units allows one to produce novel materials with unique features [2].

Among them, the nanocomposites consisting of polymer pHEMA as a matrix and TiO_2 nanoparticles as an additive are characterized with a high transparency, mechanical stability, and efficient charge separation at the organic-inorganic interface (to 50%) [2, 3]. The irradiation of the material with ultraviolet light with the photon energy that is above of the TiO_2 energy gap (>3.25 eV) leads to the electron-positron pair induction. Onward the conduction band, an electron remains localized on the inorganic component as the Ti^{3+} center. The hole transfers to the polymer. Since the recombination process is blocked, the lifetime of the photoinduced Ti^{3+} centers in this material lasts a few months [2]. The phenomenon is accompanied with the photodarkening of the medium [4]. According to the Kramers–Kronig relations, the absorption variations leads to variations of the refractive index. Thus, the measurements that considering both phenomena simultaneously should be used for the material characterization. The optimal conditions of the fabrication of samples could be found by the analysis of the optical parameters.

In this paper, we study the linear and nonlinear optical responses of the hybrids in ultraviolet (375 nm), visible (532 nm), and infrared (1064 nm) ranges as functions of the TiO_2 nanoparticles concentration.

2. Experimental Technique and Samples Characterization

The pHEMA-oxo-TiO_2 hybrids fabricated by the sol-gel technology are studied. The detailed explanation

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of the samples preparation process is described in Ref. [4]. In order to avoid the nanoparticles adhesion, we used the treatment to produce the hydrophobic surface of silica glass. The row of samples with the Ti atoms concentration from 0.88×10^{20} cm^{-3}(×1) to 17.6×10^{20} cm^{-3}(×20) has been prepared and analyzed, as well as the pure polymer matrix pHEMA (×0) (see Table 1). The thicknesses of the samples were measured by an optical microscope with a precision of about 0.1 μm.

In order to characterize the optical quality of the hybrids, we study the scattering losses into the forward hemisphere at 532 nm. The detailed description of the experimental setup and the data treatment can be found in Ref. [5]. The corresponding optical scattering indicatrices are presented in Fig. 1. It is shown that the incorporation of nanoparticles into the polymer increases the scattering of the hybrid that rises with their concentration.

The estimated scattering losses for the hybrids are presented in Table 1. It can be seen that the samples with the concentration of Ti atoms less than 8.8×10^{20} cm^{-3} are characterized with insignificant scattering losses (<6.5%). The results make these hybrids suitable for the application to photonic devices.

The NLO characterization of the samples is performed by the spatial profile analysis technique within the self-action of picosecond laser pulses at 1064 nm (42 ps FWHM) and 532 nm (30 ps FWHM) [6, 7]. The technique allows us to analyze the photoindiced variations of the absorption coefficient ($\Delta\alpha$) and the refractive index (Δn) as functions of the peak intensity of a laser pulse. The measured total ($\sim\Delta\alpha$) and on-axis ($\sim\Delta n$) transmittances are normalized on the linear transmittance of the hybrids at a corresponding wavelength. In order to extract the pure refractive response, the on-axis transmittance dependences were normalized to the total one. The samples were positioned after the waist of a laser beam. Thus, the enhancement of the on-axis transmittance indicates the positive variations of Δn. The imaginary $\mathrm{Im}(\chi^{(3)}) \sim \Delta\alpha$ and real $\mathrm{Re}(\chi^{(3)}) \sim \Delta$n parts of the cubic NLO susceptibility $\chi^{(3)}$ can be calculated within the approximation of the experimental data [7].

In order to study the accumulation processes in the hybrids, we used the continuous excitation at 375 nm. The wavelength is in the absorption band of TiO_2. Hence, we can induce the photodarkening of a hybrid due to the absorption of Ti^{3+} centers. The experimental setup was described in Ref. [3]. The analytical approach given in Ref. [8] was used for the experimental data treatment.

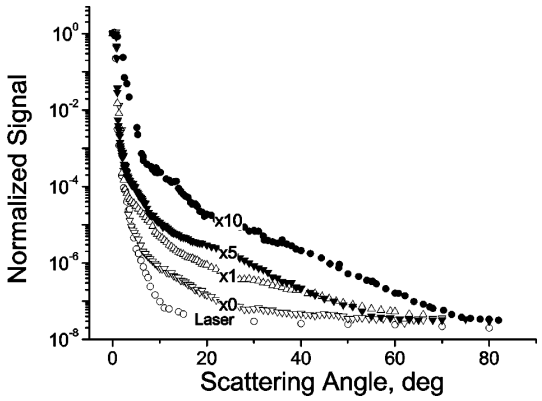

Fig. 1. Optical scattering indicatrices of the hybrids at 532 nm

3. Experimental Results

3.1. NLO response of the hybrids versus the intensity of picosecond laser pulses

The measurements of photoinduced variations of the total and on-axis transmittances as functions of the intensity of picosecond laser pulses at 1064 nm have been performed. It is shown that the nominally pure polymer demonstrates 2% of the photoinduced reduction of the total transmittance (enhancement of the absorption of the medium) with a rise of the peak laser intensity. The admixture of TiO_2 nanoparticles does not significantly affect the curves shape, while changing the efficiency of the described process. The sufficient enhancement of the photoinduced absorption (to 3.5%–4%) in comparison to pHEMA is ob-

Table 1. **Scattering losses into the forward hemisphere and thicknesses of the TiO_2-based hybrids, C – concentration of Ti atoms**

Sample	C, $\times 10^{20}$ cm^{-3}	Thickness, μm	Scattering losses, %
×0	0	137.9	3.31
×1	0.88	94.9	4.52
×2	1.76	78.1	–
×5	4.40	104.4	6.51
×10	8.80	98.6	18.17
×20	17.60	82.7	–

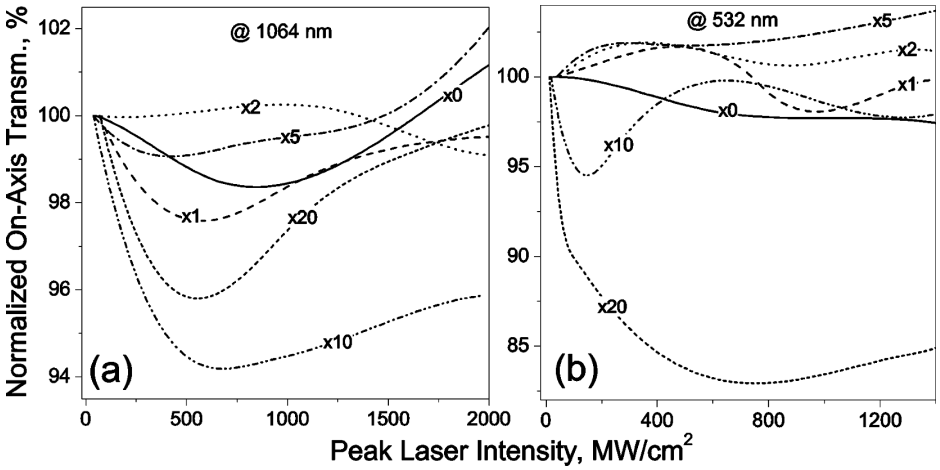

Fig. 2. Photoinduced variations of the on-axis transmittances under a self-action of picosecond laser pulses at 1064 nm (*a*) and 532 nm (*b*) for the hybrids with different Ti concentrations (notation is given in Table 1)

served at concentrations higher than 4.4×10^{20} cm^{-3} of Ti atoms.

The photoinduced variations of the on-axis transmittances for both excitation regimes are presented at Fig. 2 (each experimental curve consists of 3000 experimental points that were averaged for a clearer visualization). Under the excitation of picosecond laser pulses at 1064 nm (see Fig. 2, *a*), the refractive NLO response of the nominally pure matrix is not monotonic. The self-defocusing of the laser beam turns to the self-focusing at a peak laser intensity of ∼800 MW/cm^2. The addition of nanoparticles leads to the reduction of the intensity of the refractive index sign inversion to approximately 600 MW/cm^2. The efficiency of the mentioned processes depends on the concentration of nanoparticles. Since the enhancement of the self-defocusing effect was observed for the samples ×1, ×5, ×10, and ×20, the sample ×2 demonstrates the compensation of the pronounced phenomenon.

Table 2. **The imaginary and real parts of the cubic NLO susceptibility $\chi^{(3)}$ at different intensity ranges at 1064 nm and 532 nm for the hybrids**

Wavelength	532 nm		1064 nm	
Int. range	<100 MW/cm^2		<150 MW/cm^2	
Sample	Im($\chi^{(3)}$), ×10^{-13} esu	Re($\chi^{(3)}$), ×10^{-11} esu	Im($\chi^{(3)}$), ×10^{-13} esu	Re($\chi^{(3)}$), ×10^{-11} esu
×0	0.9	–0.8	9.4	–1.2
×1	1.4	2.0	12.4	–10.0
×2	3.1	4.9	9.5	–0.4
×5	2.6	5.5	9.1	–4.2
×10	4.7	–26.0	10.4	–21.0
×20	14.7	–72.0	23.8	–21.0

The refractive NLO response of the studied samples under the excitation at 532 nm is presented in Fig. 2, *b*. For the absorptive variations, the pHEMA total transmittance is one order less in comparison to that at 1064 nm. The observed 0.2% of the photodarkening saturates at intensities of ∼500 MW/cm^2 and turns to a slight photobleaching. The admixture of TiO_2 nanoparticles leads to the process efficiency enhancement, as it was observed for the IR excitation.

At the same time, the variations of the photoinduced on-axis transmittance are more efficient in comparison to the total one. pHEMA demonstrates the 2.5% monotonic photoinduced self-defocusing effect in the whole intensity range under study. The addition of TiO_2 nanoparticles considerably affects the refractive NLO response of the hybrids. For the samples ×1, ×2, and ×5, the photoinduced self-focusing effect was observed at the initial intensity range (<600 MW/cm^2). The efficiency of the process enhances with the concentration of nanoparticles. For the samples ×10 and ×20, the self-defocusing effect up to 16% was observed.

The calculated real and imaginary parts of the cubic NLO susceptibility are presented in Table 2. The significant enhancement of the NLO parameters for

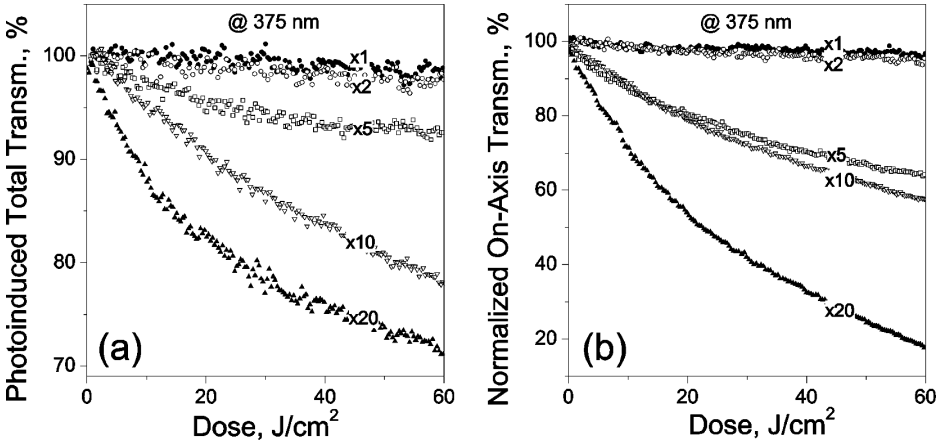

Fig. 3. Photoinduced variations of the total (*a*) and on-axis (*b*) transmittances for the hybrids versus the exposition dose of the laser irradiation at 375 nm for the hybrids with different Ti concentrations (notation is given in Table 1)

the samples ×10 and ×20 can be observed in comparison to the other samples.

The obtained results demonstrate the considerable changes of the NLO response character for the samples with concentrations of Ti atoms higher than 4.4×10^{20} cm^{-3}.

3.2. The photoinduced variations of absorption and refractive index versus the exposition dose of the CW UV laser irradiation

In order to study the photodarkening phenomenon due to the Ti^{3+} photoinduction in the hybrids, a CW laser at 375 nm was used. The photoinduced variations of the total and on-axis transmittances versus the exposition dose of laser irradiation are presented in Fig. 3 *a, b*, respectively.

The reduction of the photoinduced transmittance of samples with the rise of the irradiation dose was observed. The phenomenon is determined by the concentration of TiO_2 nanoparticles. For the characterization of the charge separation process efficiency, we apply the quantum yield η_a that shows the ratio of the amount of Ti^{3+} centers to the number of absorbed photons.

The photoinduced variations of the on-axis transmittances of the hybrids show the self-defocusing effect. The phenomenon enhances with the concentration of Ti atoms. In order to characterize the impact of a single Ti^{3+} on the photoinduced variations of the refractive index of the hybrids, we apply the parameter $a_0 = \Delta n_0/[Ti^3]$, where Δn_0 are the photoinduced variations of the refractive index, $[Ti^3]$ is the concentration of Ti^{3+} centers. The parameter describes the polarizability of a single Ti^{3+} center.

The calculated photoinduced variations of the refractive index Δn_0, the quantum yield of charge separation processes η_a, $[Ti^3]$, and the parameter a_0 for TiO_2-based hybrids are presented in Table 3.

The presented results show the maximum of the a_0 parameter at a concentration of 4.4×10^{20} cm^{-3} of Ti atoms. The reduction of a_0 at higher concentrations is accompanied with an increase of the quantum yield η_a.

4. Discussion

As it can be seen from Ref. [9, 10, 11], the NLO response of organic-inorganic hybrids consisting of

Table 3. **Photoinduced variations of the refractive index Δn_0, quantum yield of charge separation processes η_a, Ti^{3+} concentration, and a_0 parameter for TiO_2-based hybrids at 375 nm**

Sample	Δn_0 $\times 10^{-4}$	η_a, %	$[Ti^{3+}]$ $\times 10^{17}$ cm^{-3}	a_0 $\times 10^{-22}$ cm^3
×1	–0.14	12.6	0.43	–0.33
×2	–0.42	12.6	0.86	–0.49
×5	–3.20	11.3	1.91	–1.68
×10	–6.40	16.5	6.05	–1.06
×20	–10.05	20.6	13.26	–0.76

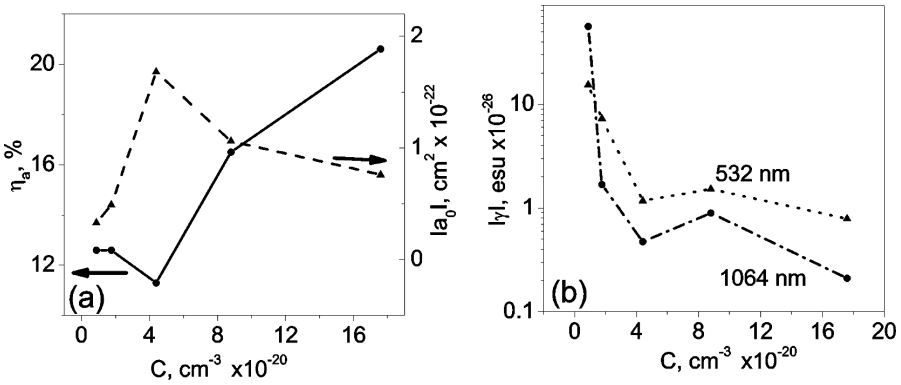

Fig. 4. The concentration dependences of the charge separation efficiency η_a, polarizability of photoinduced Ti^{3+} centers a_0 (a), and third hyperpolarizability of a nanoparticle γ for picosecond pulsed excitations at 1064 nm and 532 nm (b)

polymer PMMA with incorporated TiO_2 nanoparticles was studied by the Z-Scan technique. The excitation was performed within the femtosecond laser pulses at 780 nm and 800 nm. The concentration dependences of the estimated NLO parameters show the enhancement of the cubic NLO susceptibility up to 60 wt.% of titanium alkoxide in the precursor solution. The consequent reduction of $\chi^{(3)}$ at higher concentrations was attributed to the aggregation of nanoparticles.

In the case of pHEMA-oxo-TiO_2 nanohybrids, the NLO response concentration dependences demonstrate the significant enhancement of the parameters for the concentrations higher than 4.4×10^{20} cm^{-3} of Ti atoms. In Ref. [4], the absence of the aggregation of nanoparticles for a concentration of $8.8\times$ $\times 10^{20}$ cm^{-3} was shown by TEM microscopy. Nevertheless, at so high concentrations, the cooperative effects of nanoparticles could be observed, since the distance between them is comparable to their size.

In order to compare the influence of the cooperative effect of nanoparticles, which is observed by the NLO analysis, on the accumulation processes, we analyze the specific parameters. The concentration dependences of η_a, a_0, and the third hyperpolarizability γ of a nanoparticle are shown in Fig. 4. For the estimation of γ, the Maxwell–Garnett approximation was used. As was shown in Ref. [12], the partial contribution of the inorganic component to the NLO response of a hybrid can be calculated as

$$\chi^{(3)}_{\mathrm{TiO_2}} = \frac{\chi^{(3)} - \frac{\chi^{(3)}_{p\mathrm{HEMA}} + |F_1|F_1}{f_1}}{|F_2|F_2} f_2, \qquad (1)$$

where $\chi^{(3)}_{p\mathrm{HEMA}}$ is the contribution of the polymer matrix, f_1, f_2 are the volume fractions of the components, $F_i = \partial\tilde{\varepsilon}/\partial\varepsilon_i$, $\tilde{\varepsilon}$ is the effective dielectric function of the composite [12], and ε_i is the fraction permittivity. The volume fraction f_2 in the investigated samples varies from 0.3% ($\times 1$) to 6% ($\times 20$). The permittivities of the components are 2.1 for pHEMA and 3.6 for amorphous TiO_2, respectively. With the knowledge of $\chi^{(3)}_{\mathrm{TiO_2}}$, the third hyperpolarizability can be calculated as

$$\gamma = \chi^{(3)}_{\mathrm{TiO_2}}/(L^3 N), \qquad (2)$$

where N is the concentration of nanoparticles, and $L = 3\tilde{\varepsilon}/(\varepsilon_2 + 2\tilde{\varepsilon})$ is the local field factor. The estimation of N was done from the concentration of Ti atoms, by considering that one nanoparticle includes approximately 10^3 Ti atoms.

As can be seen from Fig. 4, b, the third hyperpolarizability γ decreases up to the Ti concentrations 4.4×10^{20} cm^{-3}. For the higher concentrations, the parameters are almost constant that could be attributed to the manifestation of the cooperative effect of nanoparticles.

For the concentration dependences of η_a and a_0, the cooperative effect leads to the enhancement of the charge separation efficiency and to the reduction of a_0.

Thus, the sample with a concentration of Ti atoms equal to 4.4×10^{20} cm^{-3} shows the optimal optical properties for the application to photonics.

5. Conclusions

We have studied the linear and nonlinear optical properties of TiO_2-based hybrids. The measurements

of photoinduced variations of the absorption coefficient and the refractive index are performed in the continuous and pulsed excitation regimes at 375 nm and 532 nm/1064 nm, respectively. The high optical quality for the samples with the concentration of Ti atoms up to 4.4×10^{20} cm^{-3} is confirmed by the analysis of scattering indicatrices. The effect of the concentration of TiO_2 nanoparticles on the NLO responses of hybrids is observed. The third hyperpolarizability of a nanoparticle was mostly constant for the samples with a Ti concentration higher than 4.4×10^{20} cm^{-3}. The effect is accompanied with the enhancement of the efficiency of the charge separation processes at the organic-inorganic interface and with the reduction of the polarizability of photoinduced Ti^{3+} centers under CW laser excitation at 375 nm. The phenomenon could be attributed to the manifestation of the cooperative effect at pronounced concentrations of nanoparticles. Thus, the concentration of $4.4\times\times10^{20}$ cm^{-3} of Ti atoms in the studied hybrids is more appropriate for the application to photonic devices.

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ЛІНІЙНА ТА НЕЛІНІЙНО-ОПТИЧНА ХАРАКТЕРИЗАЦІЯ ГІБРИДІВ НА ОСНОВІ TiO_2 ПРИ САМОВПЛИВІ НЕПЕРЕРВНОГО ЛАЗЕРНОГО ВИПРОМІНЮВАННЯ ТА ПІКОСЕКУНДНИХ ЛАЗЕРНИХ ІМПУЛЬСІВ

Р е з ю м е

Досліджено вплив концентрації наночастинок TiO_2 на оптичний та нелінійно-оптичний (НЛО) відгук гібридів на основі TiO_2. Проведено характеризацію оптичного розсіювання, фотоіндукованих змін поглинання та показника заломлення досліджених зразків. Спостерігався прояв колективних ефектів наночастинок для концентрацій атомів титану, більших за $4{,}4\cdot10^{20}$ см$^{-3}$. Явище приводить до підвищення ефективності розділення зарядів на інтерфейсі органічної та неорганічної компонент та до зменшення поляризованості фотоіндукованих Ti^{3+} центрів. Отримані результати свідчать про те, що концентрація $4{,}4\cdot10^{20}$ см$^{-3}$ атомів титану в гібриді близька до оптимальної для застосувань у галузі фотоніки.