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Effect of different types of radiation on the composition of poly(phosphazene) surface

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Changes in the composition of poly[bis(trifluoroethoxy)phosphazene] surface irradiated at λ = 6700 Å (a laser), at λ = 9.89 Å (1253.6 eV, X-ray Mg-Kα radiation), and at 4720 Å (a light emitting diode, (LED) for medical applications) were studied *in situ* by X-ray photoelectron spectroscopy. Both quantitative and qualitative changes in the surface composition compared to routine measurements of the polymer spectra are observed during an analysis of the surface upon long-term X-ray irradiation or with an increase in the X-ray radiation source power. These are the changes in the concentrations of elements and the appearance of additional states of carbon, oxygen, and nitrogen atoms. The composition of the surface irradiated with the laser and LED remains unchanged.

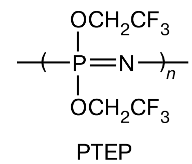
Key words: poly(phosphazene), X-ray photoelectron spectroscopy, X-ray radiation, polymer degradation, surface composition, activation energy.

Increased recent interest in studies of the effect of charged particle beams and various types of radiation on medical polymers[1—11] is due to both modification of the polymers aimed at obtaining practically valuable properties and their degradation under the ionizing irradiation. X-rays are widely used in radiography and X-ray therapy. Laser therapy is widely used in medicine during numerous surgery operations and in postoperative periods in order to accelerate the recovery of tissue surface after prosthesis. The effect of superbright light emitting diodes (LEDs) based on modern nanotechnologies on the human organism is analogous to that of laser radiation. The use of radiation in different spectral regions makes it possible to obtain diverse therapeutic effects. It is necessary to know about possible consequences of these effects on the material of implants. Since the implant surface directly contacts a living organism, the effect of physical factors on its properties is of special interest.

One of the methods providing similar information is X-ray photoelectron spectroscopy (XPS), which has been used for long to study the modification and degradation of the polymer surface under the action of various factors.[12—14] However, since XPS involves X-ray irradiation of the sample, it is necessary to estimate the applicability boundaries of this method for a chosen polymer.

An analysis of fluorine-containing polymers by XPS can be accompanied by changes in the composition of the near-surface region, which is mainly observed as a depletion of the surface in fluorine.[13] However, in spite of a wide use of XPS in studies of poly(phosphazenes),[15] knowledge on their degradation under X-ray irradiation are lacking according to our data. It is known that UV irradiation of poly[bis(trifluoroethoxy)phosphazene] (PTEP) induces photochemical reactions leading to changes in the physical properties, to the formation of volatile decomposition products, and, in some cases, to formation of cross-links.[16,17] The main products detected in the mass spectra of UV-irradiated PETP were CO_2, CH_3CF_3, and CF_3H in a 31 : 1 : 1 ratio, as well as cyclic trimers and $N_3P_3(OCH_2CF_3)_4Cl_2$ (when heated to 75 °C). The formation of CO_2 was referred to dissolved oxygen, which was hardly removed from the polymer films, and the formation of CH_3CF_3 and CF_3H was attributed to the photolytic cleavage of the O—CH_2CF_3 bond and C—C bond in the CH_2CF_3 radical, whereas the formation of cyclic trimers was caused by thermal degradation.

In the present work, the conditions under which a nondestructive XPS analysis of the surface is possible were determined, the effect of X-ray radiation on the surface composition after exceeding the critical dose was studied, and the results obtained after irradiation with a laser and a LED for medical application were analyzed.


$$\left(-\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}=N-\right)_n$$

PTEP

Poly[bis(trifluoroethoxy)phosphazene], having high bio-[18] and hemocompatibility,[19] is a promising material for biomedical

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applications,[20,21] which is mainly related to its surface properties. The necessary condition for the use of XPS for an analysis of PTEP is the determination of the critical dose after which the surface is modified. The results obtained in the present work can be used for both the determination of optimal detection conditions and the interpretation of the photoelectron spectra of PTEP.

Experimental

Linear PTEP (M = 17 400 000) with high chemical homogeneity and a low concentration of impurities (the content of residual chlorine was lower than 0.01 wt.%) were used. Poly[bis(trifluoroethoxy)phosphazene] was synthesized by condensation of poly(dichlorophosphazene) with sodium trifluoroethoxide according to a known procedure.[22] The samples studied were films cast from a 1% solution in ethyl acetate on a glass support under dry argon.

X-ray photoelectron spectra were recorded on an XSAM 800 spectrometer (Kratos, Great Britain).[23] A magnesium anode with an energy of Mg-Kα characteristic emission of 1253.6 eV (λ = 9.89 Å) was used as a source of X-ray radiation for the action on the polymer and detection of the photoelectron spectra. The polymer was also irradiated with a Mustang-2000 therapeutic laser instrument (λ = 6700 Å, power at the outlet of the light guide 25 mW, exposure time 10—30 min) and an AFS LED physiotherapeutic apparatus (red light wavelength λ = 6750 Å, radiation power 40 mW; blue light wavelength λ = 4720 Å, radiation power 80 mW; in both cases, the exposure time was 7 min).

Two different values of power dissipated at the anode of the X-ray gun were used for the detection of photoelectron spectra: 45 W (15 kV, 3 mA) and 135 W (15 kV, 9 mA). The power of 1 W corresponds to the flux of $1.54 \cdot 10^9$ photon s^{-1} cm^{-2}. In the low-power regime, the acquisition time was chosen in such a way that no visible indications of polymer decomposition be observed in the photoelectron spectra. High-resolution spectra were approximated by a Gaussian profile or the sum of Gaussians, and the background caused by secondary electrons and photoelectrons experienced energy losses was approximated by a straight line. The measurements were carried out at a pressure of ~$5 \cdot 10^{-8}$ Pa. The spectra were recorded with constant relative resolution. The energy scale of the spectrometer was calibrated by a standard procedure using the following binding energy values: for Cu $2p_{3/2}$, 932.7 eV; for Ag $3d_{5/2}$, 368.3 eV; and for Au $4f_{7/2}$, 84.0 eV (see Ref. 24). The binding energy (E_b) of the F 1s level set to be 688.2 eV as in poly(trifluoroethyl acrylate)[25] was used to compensate the charging of the sample surface and to determine the absolute position of the peaks. Quantitative analysis was carried out using atomic sensitivity factors (ASF) according to a previously described procedure.[26] The ASF values were chosen in such a way that the composition of the initial surface be corresponded to the stoichiometric formula $C_4H_4O_2F_6PN$. Since the additional state in the C 1s spectra caused by X-ray radiation appears in the region of satellites related to the non-monochromatic nature of X-ray radiation, the satellite signals were removed.

Results and Discussion

As the X-ray irradiation time increases, all spectra are shifted towards lower binding energies (E_b) due to a decrease in the surface charging induced by photoemission and the modification in the near-surface region, which results in changes in the coefficient of secondary electron emission and in the conducting properties of the sample.

The shift of spectral lines increases the error in the determination of the position of photoelectron peaks because of the absence of an equilibrium charge on the surface. This error can be decreased by shortening the acquisition time with the consecutive detection of the reference spectrum (in this case, the F 1s spectrum). Based on this, we performed similar measurements at a decreased power dissipated at the anode of the X-ray gun. In this case, the measured E_b values for C 1s, O 1s, and P 2p peaks (relative to F 1s peak) were 0.2 eV lower, whereas that of N 1s was 0.4 eV lower. The greater difference for N 1s peak is due to the fact that the N 1s spectrum was measured first, when the process of surface charging just started.

X-ray irradiation changes the elemental composition of the surface, which is manifested as a depletion of the surface in fluorine and carbon.

No impurities were revealed in the survey spectrum of the original polymer. The concentrations of elements are plotted *vs* detection duration in Fig. 1. The concentrations of phosphorus, nitrogen, and oxygen remain almost unchanged.

However, constant values of the concentrations of nitrogen and oxygen do not indicate the absence of changes in the chemical state of these elements. For example, the change in the elemental composition is accompanied by the change in the chemical state of the carbon, nitrogen, and oxygen atoms and manifests itself in the appearance of additional peaks in the C 1s, N 1s, and O 1s spectra (Fig. 2), whose intensities increase with the dose.

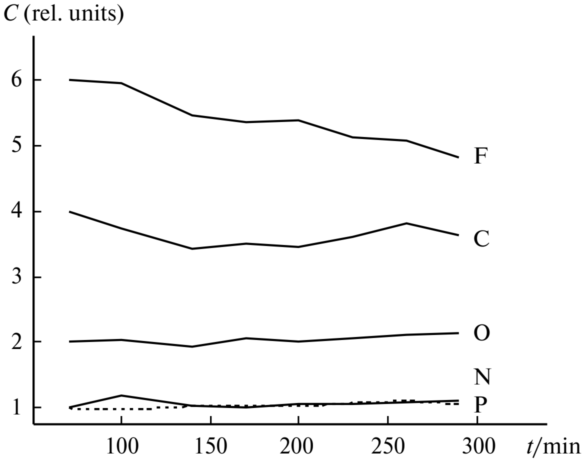


Fig. 1. Changes in the concentration of elements at different durations of X-ray irradiation. At the initial points, the concentration of each element corresponds to the stoichiometric formula.

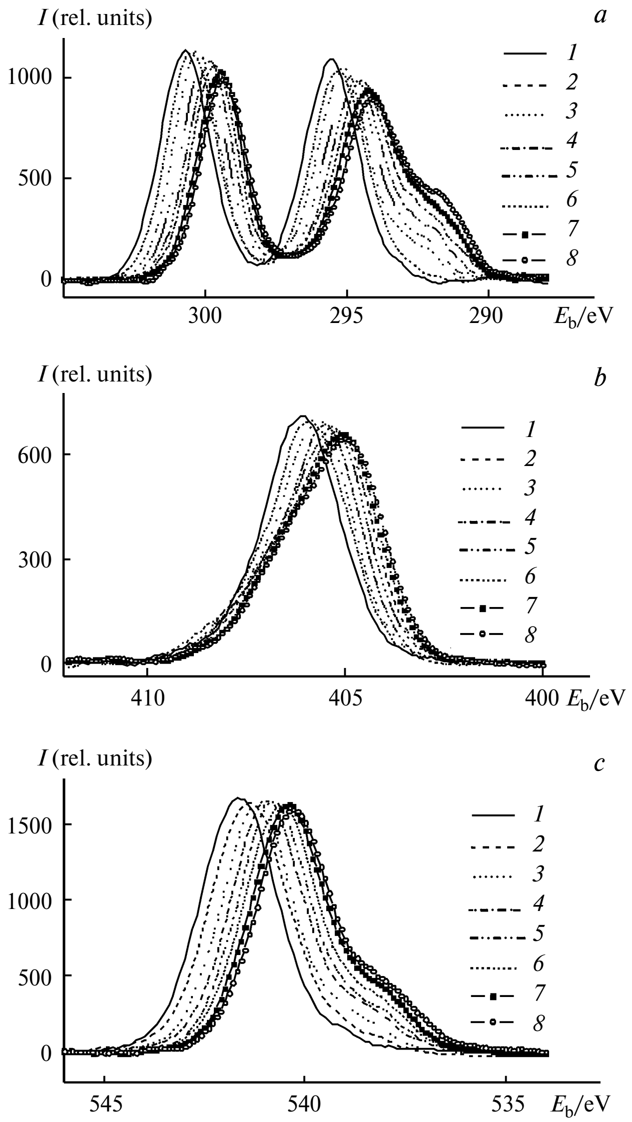


Fig. 2. Dependences of the C 1s (*a*), N 1s (*b*), and O 1s (*c*) photoelectron spectra of PTEP on the X-ray radiation dose: $1.46 \cdot 10^{13}$ (*1*), $2.08 \cdot 10^{13}$ (*2*), $2.91 \cdot 10^{13}$ (*3*), $3.54 \cdot 10^{13}$ (*4*), $4.16 \cdot 10^{13}$ (*5*), $4.78 \cdot 10^{13}$ (*6*), $5.41 \cdot 10^{13}$ (*7*), and $6.03 \cdot 10^{13}$ photon cm^{-2} (*8*).

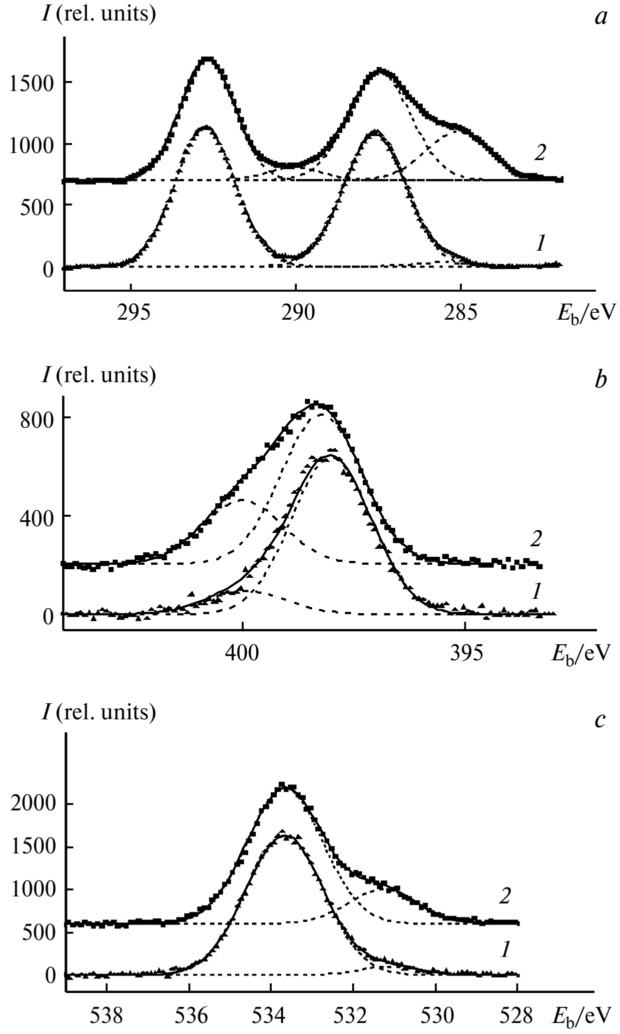


Fig. 3. The C 1s (*a*), N 1s (*b*), and O 1s (*c*) photoelectron spectra corresponding to X-ray radiation doses of $1.46 \cdot 10^{13}$ (*1*) and $6.03 \cdot 10^{13}$ photon cm^{-2} (*2*).

Figure 3 shows the results of deconvolution of the C 1s, N 1s, and O 1s spectra into components in the initial and final stages of changing the near-surface region of the sample. The C 1s spectra are presented as the sum of four states with $E_b \approx 292.8$, 290.1, 287.6, and 285.3 eV, of which the first and third values belong to the CF_3 and OCH_2 groups of PTEP. The N 1s and O 1s spectra are described by two states with $E_b \approx 398.0$ and 400.0 and 533.7 and 531.4 eV, respectively. The states with $E_b = 398.0$ and 533.7 eV belong to the N—P=N and OCH_2 groups, respectively, in the original PTEP.

The results of deconvolution of the C 1s spectra presented in Table 1 show that the concentration ratio of the OCH_2 and CF_3 groups remains unchanged, which suggests that the depletion of the surface in fluorine and carbon is mainly caused by the $O—CH_2CF_3$ bond cleavage. Elimination of the CH_2CF_3 group results in the appearance of the second component in the O 1s spectrum. The subsequent bond cleavage in the $CH_2—CF_3$ group can result in the appearance of an additional component in the C 1s spectrum with $E_b \approx 285.3$ eV corresponding to the C—C,H bonds. No spectral component with $E_b \approx 290.1$ eV is observed in the spectra of the polymers. Most likely, this component is not related to the degradation of the sample, because its characteristics remain unchanged during analysis. A more probable reason for the appearance of this component is an insufficient energy resolution.

UV irradiation of PTEP in a vacuum of $1.5 \cdot 10^{-3}$ Pa resulted in the formation of gaseous products CH_3CF_3, CF_3H, and CO_2 (see Refs 16 and 17). We do not consider the formation of CO_2 in the further analysis, because it was related to a low vacuum and the presence of oxygen in

Table 1. Changes in the relative fraction of various functional groups at different durations (*t*) of X-ray irradiation

t/min	Fraction								
	C*F$_3$	OC*H$_2$	C$_x$	C*—C,H	O*CH$_2$	O=P	N=P	NH	F
70	1.9	1.9	0	0.0	1.9	0.1	0.9	0.1	6
100	1.5	1.4	0.1	0.1	1.6	0.1	0.85	0.15	4.9
140	1.5	1.5	0.1	0.3	1.7	0.2	0.79	0.21	5.5
170	1.4	1.4	0.1	0.4	1.8	0.3	0.78	0.22	5.3
200	1.4	1.4	0.1	0.3	1.5	0.3	0.74	0.26	4.9
230	1.3	1.3	0.1	0.4	1.6	0.3	0.73	0.27	4.6
260	1.3	1.4	0.1	0.5	1.5	0.4	0.7	0.3	4.6
290	1.3	1.3	0.1	0.6	1.5	0.4	0.69	0.31	4.4

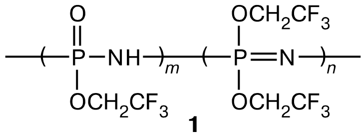
the matrix. The appearance of CH_3CF_3 and CF_3H on the PTEP surface is also improbable, because it would inevitably result in the detection in the C 1s and F 1s spectra of other peaks with binding energies different from the measured values.[24,25]

Since the P/N concentration ratio, their binding energies, and the energy interval between the P 2p and N 1s peaks change slightly during analysis, it can be concluded that the bond between phosphorus and nitrogen is retained. At the same time, the appearance of the component with $E_b \approx 400.0$ eV in the N 1s spectrum can be caused only by the cleavage of the bond between P and N and the formation of other bonds, for instance, N—C, N—H, or N—N, to which the peaks with $E_b \approx 400.0$ eV can correspond.[24] The formation of the N—C bond assumes the appearance of the corresponding component in the C 1s spectrum. Possible binding energies can range from 285.6 to 289.6 eV[24,25]; however, no additional component was observed in this range. The component with $E_b \approx 400.0$ eV in the N 1s spectrum was also observed at poly(phosphazene) modified by polyethylene—*co*-vinyl alcohol and was preliminarily ascribed to phosphazane fragments or to electrostatic interaction with the hydroxyl group.[26,27] In this case, the energy interval between the components is ~1.4 eV (*cf.* 2 eV in our case). However, we believe that poly(phosphazene) decomposed in the both cases, because the power dissipated at the anode of the X-ray gun was 300 W. The energy interval close to 2 eV was observed for the modification of poly(organophosphazene) by polyethylene—*co*-vinyl alcohol and polyvinyl alcohol.[28] Based on the dependence of the intensity ratio of both components on the copolymer used, we ascribed the state with $E_b \approx 400.0$ eV to the protonation of nitrogen by the interaction with the hydroxyl group of the copolymers. However, in our case, the O 1s spectra contain no state that could be ascribe to the hydroxyl group. In our opinion, the power dissipated at the anode of the X-ray gun (260 W) was also high. Thus, the most probable reason for the appearance of the component with $E_b \approx 400.0$ eV in the N 1s spectrum is the formation of the N—H bond.

The chemical bonds in PTEP can be arranged in the following order of increasing their dissociation energies: P—N, C—C, C—O, C—H, and P—O.[16] It follows that the N 1s and P 2p photoelectron spectra should be most sensitive to X-rays. In fact, with an increase in the irradiation dose, the first changes are observed in the N 1s spectrum in which an additional state appears from the high-energy side, whereas the P 2p lineshape remains almost unchanged during the whole experiment, which is attributed to the formation of the P=O double bond. In our opinion, this is the most probable explanation for the appearance of the additional state with $E_b \approx 531.4$ eV in the O 1s spectra, since other variants are based on the O=C—N group, which does not correspond to the states in the C 1s spectra.

An increase in the energy of the P 2p peak by 0.3 eV relative to the initial state corresponds to this assumption. Upon the electron irradiation of PTEP, the state with the energy 2 eV lower than that of the initial state was detected in the O 1s spectrum. The origin of the new state was assigned to the leaving of the CF_3 group and the formation of olefinic bonds.[16,17] However, the binding energies of O 1s and C 1s for a similar configuration do not agree with the reference data.[24,25] At the same time, the formation of P=O bonds during the pyrolysis of PTEP was observed for combined analysis by XPS and IR spectroscopy.[17] The formation of the P=O bond favors the C—O bond cleavage and, correspondingly, the formation of the volatile component CH_3CF_3 observed earlier.[16]

Summarizing all the data obtained by us and published earlier, we may propose the following scheme of chemical transformations: the P=N double bond is transformed into the ordinary P—N bond with the formation of the N—H and P=O bonds, which results in the detachment of the CH_2CF_3 group and formation of structure **1**.



$$-\!\left(\underset{OCH_2CF_3}{\overset{O}{\overset{\|}{P}}}-NH\right)_m\!-\!\left(\underset{OCH_2CF_3}{\overset{OCH_2CF_3}{P}}=N\right)_n\!-$$

1

At the maximum X-ray radiation dose, the fraction of the unit **1** formed in the polymer chain is ~30%. This value is approximately the same when it is estimated both from the C 1s, N 1s, and O 1s spectra and from the change in the fluorine concentration, thus indicating the single mechanism of conversion. However, it should be mentioned that the sequence of the process can be opposite: the detachment of the CH_2CF_3 group, the formation of the P=O double bond, the transformation of the P=N double bond into the P—N ordinary bond, and the formation of the N—H bond. Hydrogen can be released from the CH_2 group under X-ray irradiation.

After the critical dose was determined, we analyzed the effects of radiation from the laser and LED on the PTEP surface. In the case of LED, radiation with $\lambda = 6750$ and 4720 Å and the radiation power 40 and 80 mW, respectively, and the exposures of 7, 14, and 21 min were used. The duration of laser irradiation at $\lambda = 6700$ Å and a power of 25 mW was 10 and 30 min. The bond between the P and N atoms in PTEP has the lowest dissociation energy, which is close to 3.5 eV[16] and comparable to the emission energies of the LED and laser (1.8, 2.6, and 1.85 eV, respectively). It should be mentioned that the activation energy is approximately two times lower,[29] and the apparent activation energy at the initial stage of PTEP depolymerization is 1.2 eV.[30] From the quantification data it follows that the elemental composition remained unchanged relative to the original sample in all five cases. A comparison of the C 1s, O 1s, N 1s, F 1s, and P 2p photoelectron lines and the F KLL Auger lines exhibited no differences between them. The C 1s and N 1s spectra of the original polymer and the polymer after irradiations by the laser and LED are presented in Fig. 4. Thus, no changes in the elemental and chemical compositions of the PTEP surface were observed upon the irradiation of PTEP with the laser and LED in the regimes indicated above.

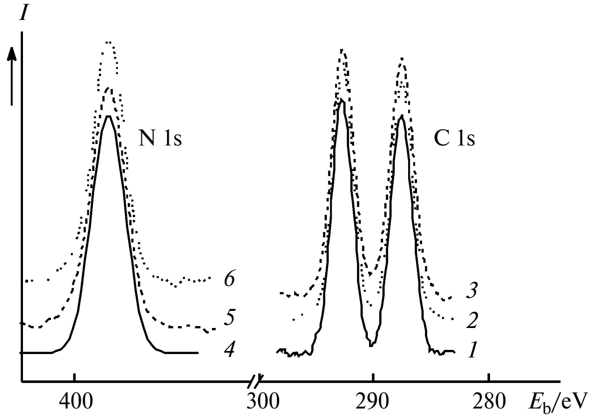


Fig. 4. Comparison of the C 1s (*1—3*) and N 1s (*4—6*) photoelectron spectra: the initial sample (*1*, *4*) and the sample after irradiation with the laser (*2*, *5*) and LED (*3*, *6*).

Thus, the possibility of radiation damage should be taken into account when analyzing PTEP by XPS. No visible decomposition of the polymer occurs within 60 min (dose $0.42 \cdot 10^{13}$ photon cm^{-2}) at a power of 45 W dissipated at the anode of the X-ray gun. At higher doses, the PTEP surface composition changes, which is expressed in detachment of the CH_2CF_3 groups and the transformation of the P=N double bonds into ordinary bonds to form P=O and N—H bonds. At a dose of 135 W, about 30% of the polymer is transformed within 290 min ($6.03 \cdot 10^{13}$ photon cm^{-2}).

When determining the energy position of the photoelectron peaks, one should take into account that the photoelectron lines are continuously shifted for a long time (290 min) due to the absence of the equilibrium charge state on the PTEP surface.

It was experimentally shown that laser and LED irradiation of PTEP in the regimes used in medical practice does not change the elemental and chemical compositions.

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