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MIGRATION OF OPTICAL EXCITED STATES OF THE MODIFIED CHROMIUM COMPLEXES OF COLLAGEN

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Photoluminescent properties of the collagen modified by chrome complexes are investigated. The analysis of the spectra of a photoluminescence at excitation in ultra-violet area shows that intrinsic photoluminescence of collagen undergoes a quenching with the increase of content of chromic complexes. In the modified collagen luminescence ranges are also deformed with full quenching of phenylalanine peak. The kinetics of decay of a photoluminescence of samples of the native and modified collagen, samples of phenylalanine and a tyrosine is measured. With the increase of content of chrome complexes in the modified collagen there is a redistribution of the dominating role of the radiating centers of collagen from the phenylalanine residue to tyrosine residue.

Keywords: Photoluminescence, collagen, phenylalanine, tyrosine, chrome, quenching.

INTRODUCTION

In [1] were represented optical properties of native collagen. Optical properties of native collagen are determined by presence of aromatic amino acids such as phenylalanine, tyrosine and tryptophan. Earlier [2] it was shown that the fluorescence spectra of native collagen excited in the near ultraviolet and visible regions have of excimer nature and are determined by presence of phenylalanine, tyrosine. Recently in [3] were discussed the nature of fluorescence of carbon containing nanostructured objects including collagen. In the present work, it was experimentally found that when excitation of collagen occurs in the near ultraviolet region of the spectrum in the presence of chromium complexes in the fibrous structure of collagen, the quenching of the excimer fluorescence of collagen is observed. When the collagen is modified by chromium complexes, the shape of the photoluminescence (PL) spectra, its half-width and the position of the maximum are changed, and the screening of the exciting radiation by chromium complexes is the dominant mechanism of quenching of collagen luminescence.

This circumstance is due to the fact that in the near ultraviolet region of the spectrum the values of the absorption coefficient of light by impurity centers, chromium complexes, considerably exceed the values of the absorption coefficients of the radiating collagen centers.

1. Materials and methods

Samples for the study of collagen modified with chromium complexes (CMCC) were prepared according to the standard method for natural chrome tanned leathers [4]. As a control drug, a sample of native collagen (NC) was used. Determination of chromium content in the samples (CMCC) was carried out according to the method developed earlier [4]. The PL spectra and kinetics were measured on a DFS-12 unit with an FEU-100. PL excitation was carried out by the emission line of 337 nm of the nitrogen laser LGI-505. The measurements were carried out at room temperature.

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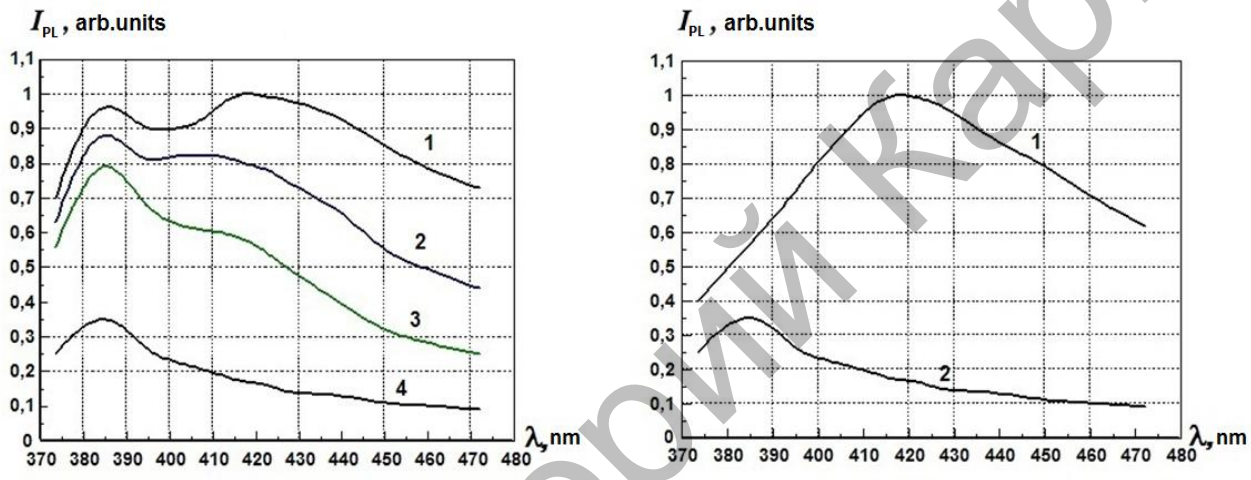
Below, we present experimental data of the effect of chromium complexes on the behavior of excimer luminescence of collagen upon excitation in the near ultraviolet region of the spectrum. Fig. 1 (a) shows the photoluminescence spectra of CMCC samples with different mass content of chromium (in terms of chromium atom) with the ND spectrum. As can be seen from the figure, the spectrum of native collagen is a broad band with two maxima at 384 and 417 nm.

An increase in the chromium content leads to deformation of the CMCC spectrum due to quenching of the long-wave band with a maximum of 417 nm, and in the sample with a maximum chromium content (1.1%), the PL spectrum is represented by one bell-shaped band with a maximum at 384 nm. As it was shown earlier [3] aromatic residues of phenylalanine participates mainly in the formation of PL spectra of collagen in the visible region of the spectrum with a maximum at 417 nm at the exciting the 337-nm line.



a) b)

Fig.1. PL spectra at λ_{ex} = 337 nm of a-samples of CMCC with different chromium content: NC 1-0%, 2-0.1%, 3-0.6%, 4-1.1%; b-phenylalanine (1) and tyrosine (2).

To establish the origin of the PL band of native collagen with a maximum at 384 nm, we performed additional measurements of the shape of the PL spectra of preparations of phenylalanine and tyrosine, whose aromatic residues can form excimer centers in the fibrous structure of collagen. These experimental data are presented in Fig. 1 (b). Comparison with the spectra of PL preparations of phenylalanine and tyrosine in Fig. 1b allows us to identify these maxima at 384 and 417 nm with the maxima of the spectra of tyrosine and phenylalanine, respectively. Comparison of the curves shown in Fig. 1 (a) and 1 (b), allows us to conclude that the ultraviolet luminescence band of collagen with a maximum at 384 nm is due to the excimer luminescence of tyrosine residues.

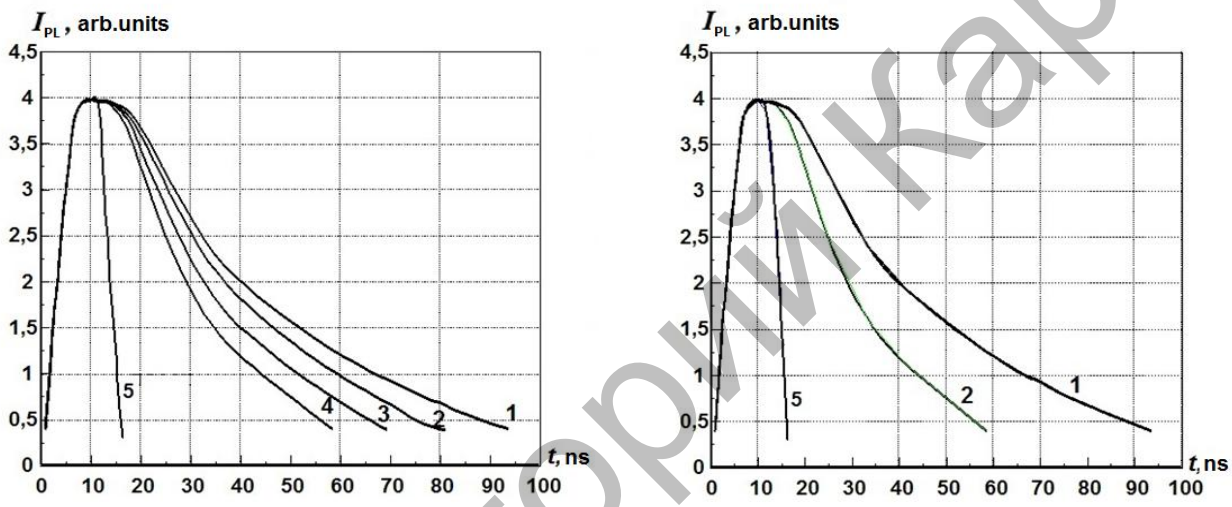
An additional analytical characteristic for the identification of PL spectra is the measurement of the kinetics of PL decay. Therefore, we measured the kinetics of the fluorescence decay of the samples of NC, CMCC, phenylalanine and tyrosine preparations. It was shown in [3] that the kinetics of tyrosine fluorescence is characterized by shorter times than for phenylalanine. The ones shown in Fig. 2 (a) and 2 (b), the curves show that an increase in chromium in CMCC samples leads to a transition from the "phenylalanine" kinetics of PL decay to "tyrosine" and, accordingly, to a shortening of the characteristic PL damping time from 10 ns to 5 ns.

The obtained experimental data allow to draw a conclusion that in collagen there are two types of excimer-forming centers - physical dimers formed by the residues of phenylalanine and tyrosine residues.

In samples of CMCC with an increase in the chromium content, the dominant role of the learning centers of collagen from the phenylalanine residue to the tyrosine residue is redistributed. In the CMCC samples with the maximum chromium content (1.1%), the luminescence of the phenylalanine "excimers" is completely extinguished.

2. The discussion of the results

To explain the experimental data obtained, we carried out the following analysis. It is known [5-6] that chromium complexes almost do not absorb light in the near ultraviolet region (250-400 nm), but they have an intense wide characteristic absorption band from 400 to 500 nm. Consequently, the redistribution of the dominant role of the radiating centers of collagen from the phenylalanine residue to the tyrosine one is due precisely to the absorption characteristics of the chromium complexes. The picture of the process can be represented as follows.



a) b)

Fig.2. The kinetics of PL decay at λ_{ex} = 337 nm of CMCC a -samples with chromium content: 1-0%, 2-0.1%, 3-0.6%, 4-1.1%, 5-laser; b -phenylalanine (1) and tyrosine (2).

When the native collagens sample is illuminated, light quanta are absorbed by both "phenylalanine" and “tyrosine” excimer-forming centers. The relaxation of the excited state of these centers (decay of the excimer) leads to the formation of a luminescence of collagen. In the CMCC samples, the visible luminescence of the "phenylalanine" excimers is absorbed (internal screening) by chromium complexes, and at the maximum chromium concentration we observe complete quenching of the luminescence of the "phenylalanine" excimers.

Conclusions

Investigation of the spectra and kinetics of PL decay of the native and collagen-modified chromium complexes has made it possible to draw a conclusion about the mechanism of quenching of luminescence in modified collagen consisting of energy migration from the phenylalanine to the tyrosine center of luminescence.

The research of these objects is related to the prospects of application due to a unique combination of a number of key properties including tunable photoluminescence, important for the development of tunable lasers, as well as biomedical applications where photostability, biocompatibility, molecular dimensions are essential, allowing a chemical connection with any biomolecule, without jeopardizing its function.

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