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Studies of Melanin Pigments of Different Origin

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Absorption spectra and spectra of time-resolved and stationary photoluminescence (PL) measured at low and room temperatures have been investigated for the water-soluble and water-insoluble forms of a melanin pigment, as well as melanin extracted from human hairs whose color is defined by the melanin content.

The results obtained can be explained by a complexity of the melanin structure which has, probably, conjugated linear parts and clustered parts with different physical properties.

Keywords: absorbance; biopolymer; melanin; pigment; photoluminescence

INTRODUCTION

Melanin is a pigment playing an important role in alive organisms including human ones. Namely, melanin is responsible for UV protection of skin, eyes, and hairs, melanin in inner ear regulates keenness, and melanin granules are present in the central nervous system (their precise role is unclear). Diseases connected with melanin are following: skin cancer (melanoma), deafness, Parkinson's disease.

The clarification of physical processes in melanin as well as properties of this pigment, in particular its electronic structure, is both the way to use this material in molecular electronics and the key to understand the role of melanin in human organism.

Melanin pigments are macromolecular polymers which are formed by oxidation of phenols, mainly catechols, 3,4-dihydroxyphenylalanine,

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5,6-dihydroxyindole. Both natural and synthetic melanins have applications in many fields. The chemical structure of natural melanins still remains vague due to a very complicated polymer structure.

Nevertheless, all melanins have a number of common structural features that make them similar to amorphous semiconductors [1,2]. First of all, this is a periodic polymer structure and the presence of π-conjugated parts in this structure. Therefore, electronic properties of melanin pigments can be studied spectroscopically [3].

We study the absorption spectra of time-resolved photoluminescence (PL) for solutions and films of water-soluble (WS) and water-insoluble (WI) natural plant melanins [3] as well of the melanin pigment extracted from human hairs of a brown color.

EXPERIMENTAL

The main used technique was PL spectroscopy [4]. Stationary and time-resolved PL spectra were measured with the help of a setup based on an MDR-12 monochromator (LOMO) equipped with the photoelectric system and via an interface card connected with PC. The spectral width of the split during PL studies was 0.2–0.4 nm. PL was excited by pulses of a nitrogen laser with wavelength of 337.1 nm. The duration of a laser pulse was 9 ns, frequency of pulses was 100 Hz, and intensity of pulses was 5 kW. To register the kinetic and time-resolved PL spectra, the stroboscopic system with "time window" equal to 0.1 ns was used. This allowed us to measure PL spectra with different delay times t_d with respect to a laser pulse. The time resolution of the setup in measurements of PL spectra was 0.7 ns and was defined by the front steepness of the laser pulse. The time resolution of the PL kinetics was equal to the width of an oscilloscope strobe (0.1 ns).

We study following melanins [3]: water-soluble (WS), water-insoluble (WI) natural plant melanins [3] as well of the melanin pigment extracted from human hairs of a brown color. To prepare a solution and suspensions of WI melanin, we used its property to be dissolved well in alkalies. Small-size colloid particles were formed in such a solution after water adding. Then these particles were precipitated and can be used after cleaning in the investigation. Nanostructured colloid particles of WI melanin can form homogeneous water solutions. These solutions have PL on the contrary to the original melanin untreated by alkali. Colloid layers deposited on quartz substrates formed thin uniformly colored films. In an analogous manner, human hairs were dissolved in a 5% solution of NaOH, and then a dark brown pigment of melanin can be extracted by water adding.

RESULTS AND DISCUSSION

Absorption Spectra

The main parameter which characterizes optical properties of amorphous semiconductors is the edge of optical interband absorption described by the Tauc's equation [5]

$$(\mathrm{E}\alpha)^{0.5} = \gamma(\mathrm{E} - \mathrm{E_g}) \tag{1}$$

where E – photon energy, $\mathrm{E_g}$ – optical band gap, α – absorption coefficient, and γ – constant.

Figures 1 and 2 show the absorption spectra of a water solution of melanin and films of WS and WI melanin. It can be seen that a linear dependence is observed in the $(\mathrm{E}\,\alpha)^{0.5} \propto \mathrm{f(E)}$ coordinates, and the extrapolation to the E axis gives the value of band gap $\mathrm{E_g} = 1.4$ eV. The main parameter that can lead to the amorphization of the polymer in a solution is the length distribution of π-conjugated fragments of the polymer. Two models of melanin packing were proposed in [6]: a linear model and a stacking model. A π-conjugated fragment consisted of n

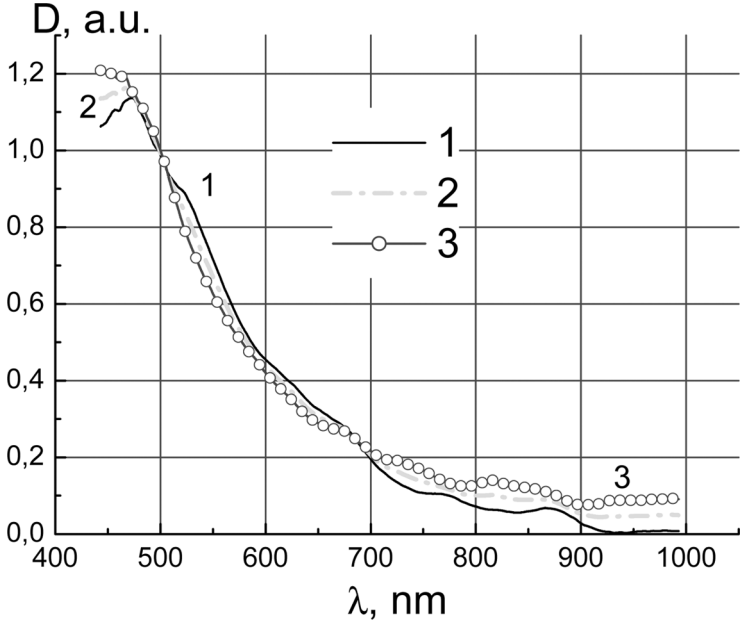

FIGURE 1 Absorption spectra of solution (1) and films of WS (2) and WI (3) melanins.

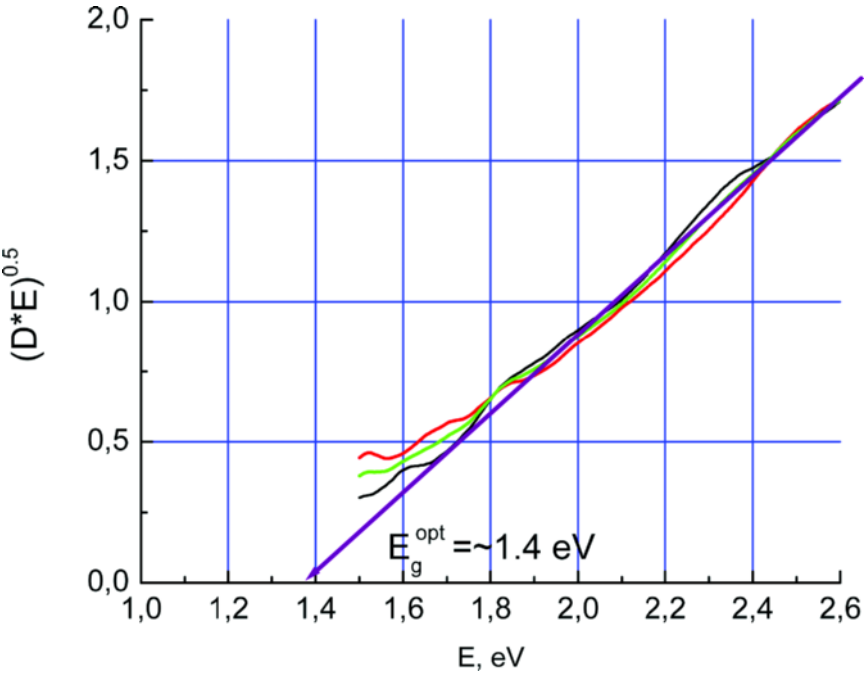

FIGURE 2 Tauc's plot and estimation of E_g.

benzene cycles such as that in PPP-polymer can be distinguished in a chromophore in the linear model. Obviously, a change in n should lead to E_g fluctuations.

PL Spectra

On the other hand, the study of the temperature dependence of PL shows that, in a solution, it is possible the formation of pre-dimeric structures, which is characteristic of the stacking model of packing of chromophores. Such structures can give both monomeric and excimeric irradiation in PL spectra. As a rule, monomeric PL has shorter time of life comparing to excimeric one and is shifted to the short wavelength side. Excimeric radiation is observed in time-resolved PL spectra at higher t_d values. The stationary PL spectra of water solutions of WS melanin at different concentrations are presented in Figure.3 (curves 1–4). It is obvious that a change of the melanin concentration doesn't lead to significant changes in PL

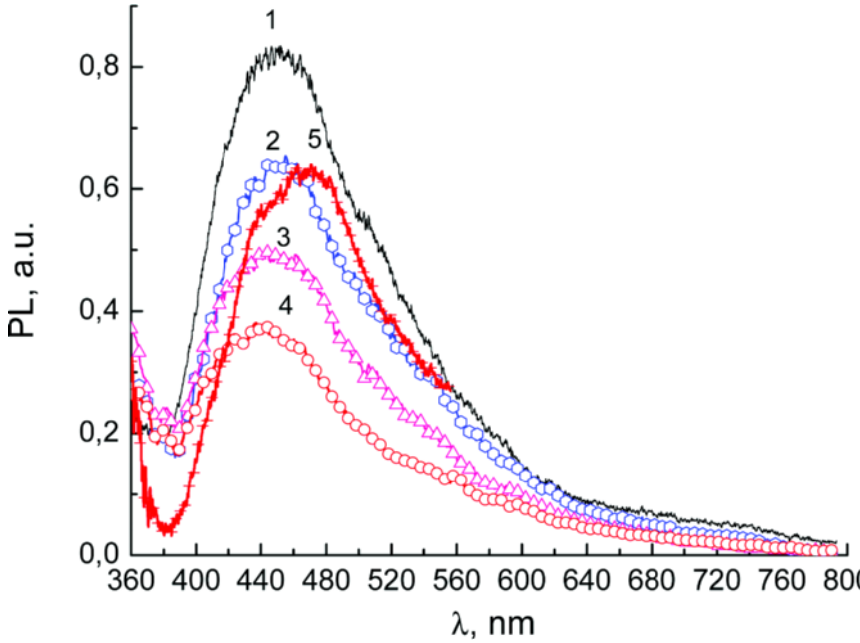

FIGURE 3 Stationary (1–4) and time-resolved (5) PL spectra of WS melanin of different concentrations at 300 K. (1–4)-C = 10^{-2}; 10^{-3}; 10^{-4}; 3.10^{-5} g × cm^{-3}. (5)-C = 3.10^{-5}g × cm^{-3}, t_d = 5 ns.

spectra. The maximum of PL is shifted from 450 to 440 nm at the short wavelength side with decrease in the concentration. This phenomenon can be explained by the fluctuation of π-conjugation in interacting chromophores. For the time-resolved PL spectrum (curve 5, $t_d = 5$ ns, C = 10^{-2}g × cm^{-3}), a sufficient decrease of the PL intensity at the short wavelength part and a shift of the spectrum to the long wavelength side are observed. This is characteristic of excimeric luminescence.

The excimeric character of long wavelength luminescence is also confirmed by low-temperature studies. Figure 4 shows stationary (curves 1, 2) and time-resolved (curves 3, 4) PL spectra of WS melanin at 300 K (curve 1) and 4.2 K (curves 2–4). It can be seen that the wide unstructural component of PL is quenched with decrease in temperature, and the spectrum is shifted to the short wavelength side. The shape of the low-temperature PL spectrum depends on t_d. Such a behavior of PL spectrum can be explained as follows: the formation of excimeric states is complicated at low temperature, and

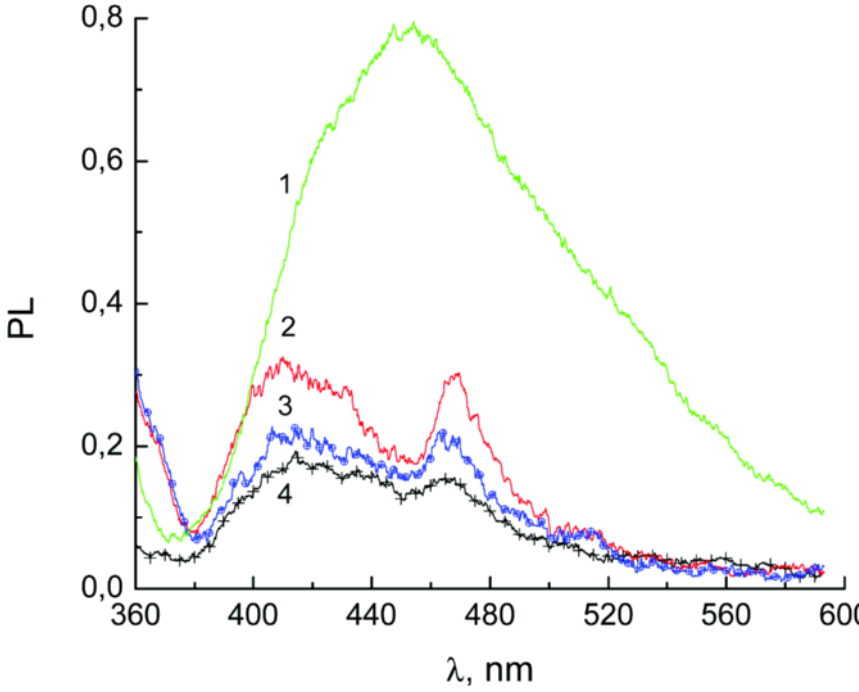

FIGURE 4 Stationary (1, 2) and time-resolved (3, 4) PL spectra of WS melanin. $C = 3.10^{-2} g \times cm^{-3}$ at 300 K (1) and 4.2 K (2–4). Curve 3-$t_d = 0.7$ ns, ns, curve 4-$t_d = 10$ ns.

the monomeric luminescence of separate chromophores is observed in the spectrum. The observed structure (bands at 409 and 467 nm) can be connected with different n values of π-conjugated cycles.

The PL spectra of WI melanin films at 77 K (curves 1, 2) and 300 K (curves 3–5) are presented in Figure. 5. A decrease in temperature leads to a significant PL quenching at the short wavelength part and to a shift of the spectrum to the long wave-length side, as it was in the case of solutions. With decrease in temperature from 300 to 77 K, the maxima of bands of the stationary spectra are shifted from 460 to 410 nm. The decrease in the PL intensity by the order is also observed. The redistribution of the intensity of bands and their shift to the short wavelength side are observed at the decrease of t_d from 5 ns (curve 4) to 0.7 ns (curves 2, 3). The observed changes in the PL spectra of WI melanin films also can be explained by the manifestation of monomeric and excimeric

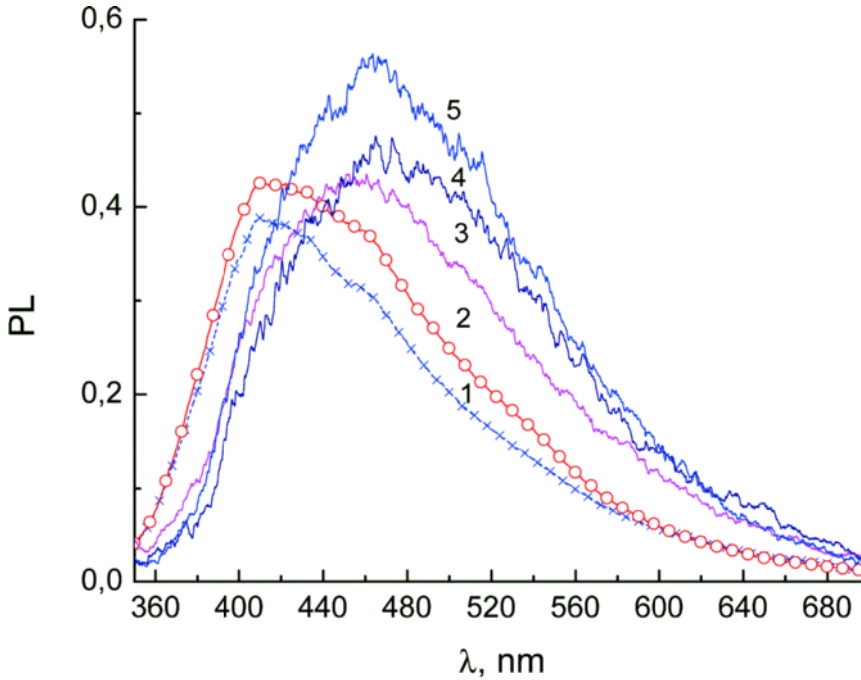

FIGURE 5 Stationary (1, 5) and time-resolved (2–4) PL spectra of WI melanin at 77 K (1, 2) and 300 K (3–5). Curves 2,3-$t_d = 0.7$ ns, curve 4-$t_d = 5$ns.

luminescence. PL of these films at room temperature is mainly excimeric. The lifetime of PL of studied melanin films at room temperature dependent on the wavelength of radiation changes from 1.8 to 2.2 ns. The lifetime in the band at 410 nm increases to 4 ns during the temperature change from 300 K to 77 K.

Figure 6 is the comparison of the stationary PL spectra of WI melanin (curve 1), WS melanin (curve 2), and melanin extracted from human hairs (curve 3) in a 5% solution of NaOH. It is clear that the spectra of WS and WI melanins are similar and have maximum at ca 460 nm. The lifetimes of PL for these melanins at the band maximum are approximately equal to 3.2 ns.

For the melanin extracted from human hairs, the maximum is located at 440 nm, and the lifetime is equal to 2.4 ns. The luminescence, which in the other melanins is observed for short lifetimes $t_d = 0.7$ ns, manifests itself in the stationary PL spectrum of the melanin extracted from hairs.

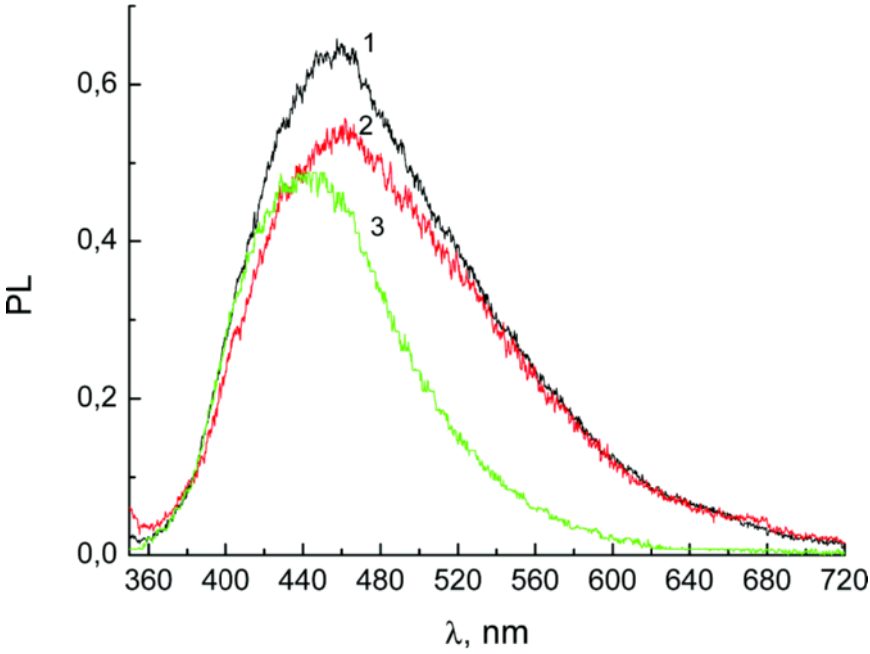

FIGURE 6 Stationary PL spectra of solutions of WI melanin (1), WS melanin (2), and melanin extracted from human hairs (3) in a 5% solution of NaOH.

CONCLUSIONS

1. Absorption spectra of solutions and films are very similar and described well by the Tauc's model characteristic of substances with amorphous disordered structure.
2. PL spectra are defined by the length of π-conjugation and by the formation of pre-dimeric structures, which leads to both monomeric and excimeric PL manifestations. The spectral distribution of monomeric PL is connected with the length of π-conjugation of chromophores. The presence of excimeric PL can be explained by the formation of stacked pre-dimeric structures.
3. The lifetime is $\sim$2–3 ns at room temperature and increases to 4 ns at 77 K.
4. The results obtained can be explained by complexity of the melanin structure which, probably, has conjugated linear parts as well as clustered parts with different physical properties.

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