The Study of Ordered Melanin Films

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Two types of melanin films: self-arranged ordered films and amorphous films have been studied in the present paper. The structure, absorption spectra, spectra of photovoltage, and spectra of time-resolved photoluminescence have been investigated for both types of melanin films. Time-resolved photoluminescence was measured at room temperature at different delay times.

The reason for the difference in the electronic properties of structurized and amorphous films of melanin is attributed to the structural features of the films related to ordered dendrite-like structures and amorphous disordered ones, respectively.

Keywords: absorbance; biopolymer; melanin; photoluminescence; self-arrangement

INTRODUCTION

Melanin is a pigment playing an important role in alive structures including human organisms; in particular, it is a protector of human hairs and skin from UV. The clarification of physical processes in melanin, as well as properties of this pigment, in particular the electronic structure, is the key to understand the role of melanin in human organism.

In previous papers [1,2], we concluded that the regions of stacked nanoclusters could be formed in the film of biomolecular semiconductor melanin. The co-existing of ordered and disordered areas defines the unusual physical properties of studied melanin films [1,2].

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

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 [3]. First of all, this is a periodic polymer structure and the presence of π-conjugated parts in this structure. Therefore, the electronic properties of melanin pigments can be studied spectroscopically [4].

In present work we study two types of melanin films: "structurized" ordered films and quasiamorphous ones.

EXPERIMENTAL

Photovoltage was measured by the Bergman method improved by Akimov [5]. According to this technique, a sample is isolated from other electrode, an ITO layer deposited on the polished quartz substrate, by a transparent dielectric film of 10–20 μm in thickness. Under illumination of such cells by light pulses of a duration t_l, a difference of potentials, the "capacitory" photovoltage, arises between the illuminated and dark surfaces of the cell. The alternate voltage on a loading resistance is measured by an experimental setup.

The measurement setup is as follows: light from a 120-W iodine tungsten lamp («Hitachi») via systems of quartz lenses, a chopper (a modulation frequency is 80 Hz), and a corresponding filter is focused on the slit of a monochromator MDR-4 (LOMO). Monochromatic light then is focused onto the window of an electrically screened measurement cell, at the center of which the sample is placed. Photovoltage is measured by a lock-in nanovoltmeter «Unipan-232B» with a preamplifier "Unipan-233-7". The signal from an optronic pair mounted on a chopper is used as a reference for the lock-in. The experimental data with the help of an ET-1050 interface card are digitized and collected in PC.

After each series of measurements, the spectral distribution of a lamp was measured by a calibrated pyroelement, and the photovoltage spectra were normalized onto the equal number of incident photons.

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 [5]. 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 a wavelength of 337.1 nm. The duration of a laser pulse was 6 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 a "time window" equal to 0.1 ns was used. This allowed us to measure the PL spectra with different delay times t_d with respect to a laser pulse. The time resolution of the setup in the measurements of the PL spectra was 0.7 ns and was defined by the front steepness of a laser pulse. The time resolution of the PL kinetics was equal to the width of an oscilloscope strobe (0.1 ns).

The absorption spectra were measured by a serial "Hitachi" spectrophotometer equipped by a PC module.

The melanin substance was extracted from a plant raw material [1,2]. We study the following melanin films: self-arranged ordered films were obtained at some characteristic concentration from an aqueous solution by wedge-shaped dehydratation, and amorphous films were obtained as described earlier [2] from a water-alcohol mixture. The films of both melanin types were deposited on two types of substrates: quartz substrates used for studying the absorption and PL; and ITO-coated substrates used for studying the photovoltage.

To make the images of obtained films, a serial "Olympus" mark BX-51 polarized microscope equipped by CCD camera was used. The images were made with 150x magnification.

RESULTS AND DISCUSSION

Morphology of the Films

Figure 1 shows the images of ordered (a) and disordered amorphous (b) melanin films obtained by a CCD camera equipped with a polarized microscope with crossed polarizers. It can be seen that the ordered film
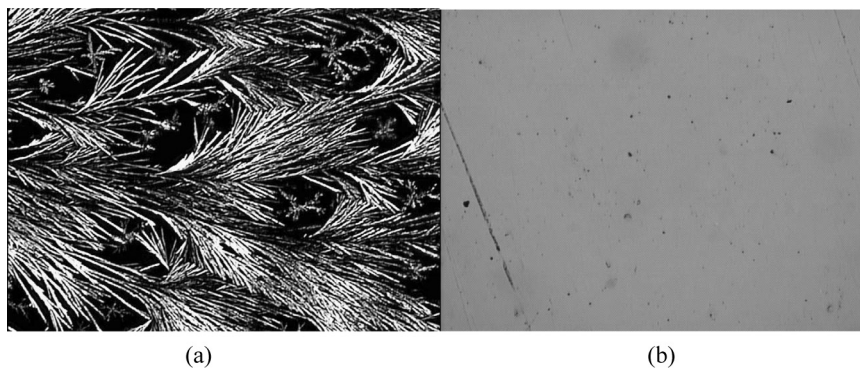

(a)   (b)

FIGURE 1 Images of ordered (a) and disordered amorphous (b) films of melanin.

has dendritic structure, whereas the amorphous film has no visible structure. The estimation of the dendrite parts sizes showed that the average branch is of hundreds of nanometers in thickness (diameter) and up to 100 μm in length. The total size of a single dendrite is up to 1 mm on the whole, and these dendrites are seen well visually without a microscope.

Absorption Spectra

Figure 2 shows the absorption spectra of ordered and amorphous films of melanin. The shape of the absorption spectra in the visible region for all samples was a slow monotonic decay from 375 to 1000 nm with the weak features: the shoulder at ~ 510 nm and bands in the weak absorption region (600–850 nm) for structurized ordered films.
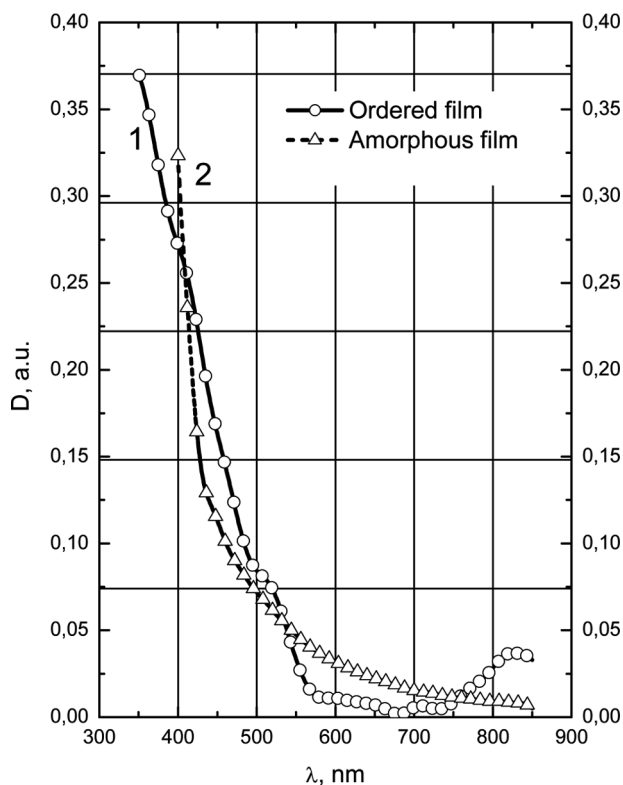

FIGURE 2 Absorption spectra of ordered (1) and amorphous (2) melanin films.

The main parameter which characterizes optical properties of amorphous semiconductors is the optical interband absorption edge described by the Tauc's equation [7]

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

where E-photon energy, E_g-optical band gap, α-absorption coefficient, and γ-constant.

The linear dependence is observed in the $(E_\alpha)^{0.5} - \propto f(E)$ coordinates. According to the procedure described in [2], the extrapolation to the E axis gives the value of band gap $E_g = 1.4$ eV for the disordered amorphous film, and $E_g = 1.1$–1.2 eV for the arranged one.
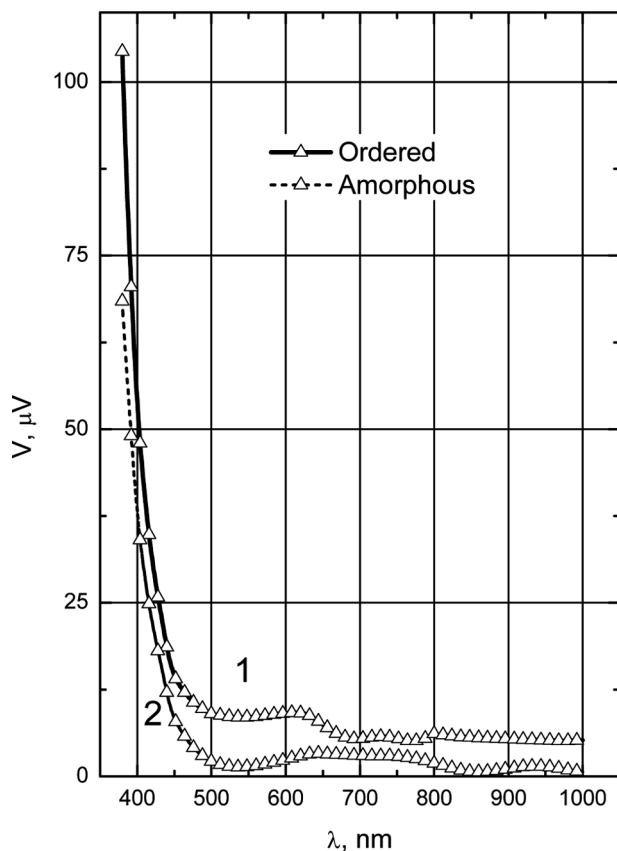

FIGURE 3 Spectra of photovoltage of ordered (1) and amorphous (2) films of melanin.

Spectra of Photovoltage

Figure 2 shows the photovoltage spectra of ordered (1) and amorphous (2) films of melanin. The shape of the photovoltage spectra corresponds, on the whole, to the shape of absorption spectra. It should be noted that the value of photovoltage is sufficiently greater for ordered than for amorphous films both in the regions of strong and weak absorption.

PL Spectra

Figure 4 shows the spectra of time-resolved photoluminescence measured without delay (time of delay $t_d < 1$ ns) of ordered (1) and amorphous (2) films of melanin. The excitation was executed by a nitrogen laser at $\lambda_e = 337$ nm, $\tau = 6$ ns. Figure 5 shows the spectra of time-resolved photoluminescence measured with delay (time of delay > time of excitation) of ordered (1) and amorphous (2) films of melanin.

With regard for the previous results of the study of time-resolved PL for different melanin types at room and lower temperatures [1,2], the analysis of Figures 4 and 5 indicates that:

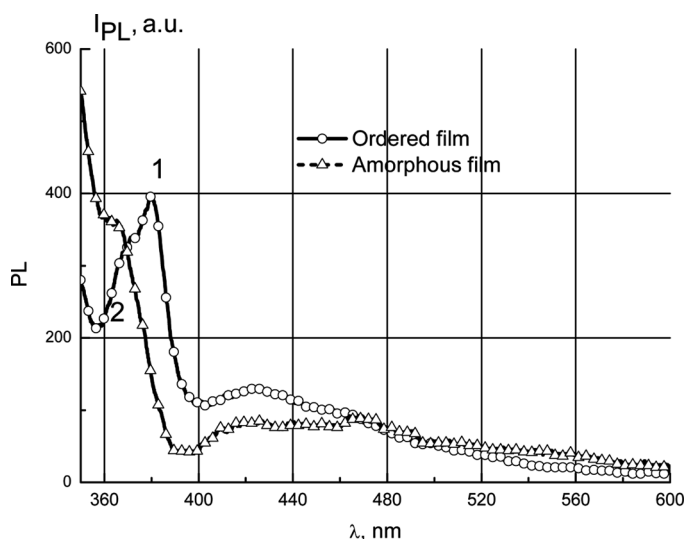1) the band at ca. 364 nm is a molecular band, i.e., it is caused by molecular irradiation;

FIGURE 4 Spectra of time-resolved photoluminescence measured without delay ($t_d < 1$ ns) of ordered (1) and amorphous (2) films of melanin. The excitation by a nitrogen laser at $\lambda_e = 337$ nm, $\tau = 6$ ns.
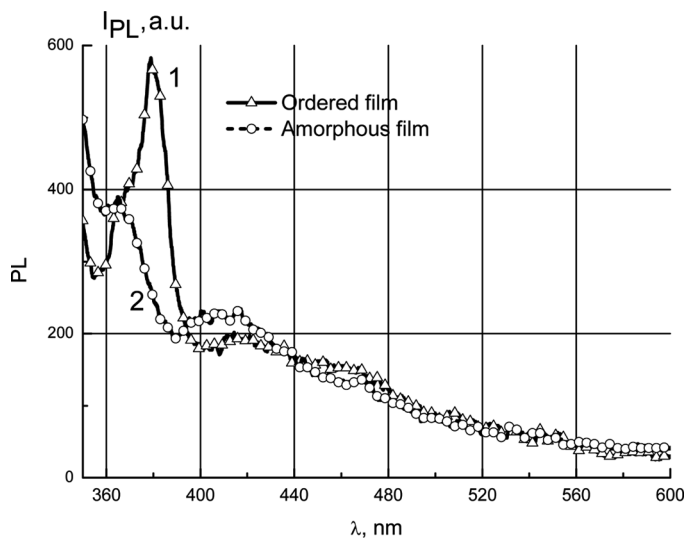
FIGURE 5 Spectra of time-resolved photoluminescence measured with delay $(t_d > \tau)$ of ordered (1) and amorphous (2) films of melanin. The excitation by a nitrogen laser at $\lambda_e = 337$ nm, $\tau = 6$ ns.

2) at the range >400 nm, the excimeric irradiation by pre-dimeric states is observed for quasiamorphous films;

3) pre-dimeric states become physical dimers for ordered films. The lifetime for these states is shorter than that for excimeric states. They are observed at short excitation times <1 ns;

4) The main difference between ordered and quasiamorphous films, namely the appearance of a new intense band at 380 nm, can be explained as follows: the formation of dendrite-like structures leads to a significant growth of the linear parts of the melanin polymer. As was described earlier [1,2], such bands in the short-wavelength region are characteristic of the linear melanin stacking arrangement.

CONCLUSIONS

1. The absorption and photovoltage spectra in the visible region show a slow monotonic decay for all samples from 375 to 1000 nm with the weak features (bands) for structurized films.

2. The extrapolation of the linear dependence in the $(E_\alpha)^{0.5} \propto f(E)$ coordinates to the E axis gives the value of band gap $E_g = 1.4$ eV for disordered amorphous films and $E_g = 1.1$–1.2 eV for arranged ones.

3. The value of photovoltage is strongly greater for ordered than for amorphous films.

4. The maximal difference between two types of the studied samples was observed in PL. The intense band with the maximum at ca. 380 nm is observed for ordered films, and this band is not observed for amorphous films. The appearance of this new intense band can be explained by the formation of dendrite-like structures, which leads to a significant rise of the average length of the linear parts of the melanin polymer.

5. Thus, the general reason for the difference in the electronic properties of structurized and quasiamorphous films of melanin is attributed to the structural features of the films related to ordered dendrite-like clusters and amorphous disordered structures, respectively.

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