

Optical Absorption and Luminescent Properties of Melanin Films

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Abstract—The optical absorption and luminescence spectra of the films of natural melanin were measured. The results are explained based on a nanocluster structure of the films. © 2002 MAIK “Nauka/Interperiodica”.

The natural pigment melanin plays an important role in living organisms, including humans. In particular, melanin acts as a UV protector and participates in many physiological and psychic processes. However, the mechanism of the interaction of this compound with UV radiation, as well as the contributions of melanin to complicated processes, is still unknown. Knowledge of the physical properties, including the electron structure, of melanin is probably a key to understanding the role this compound plays in the human organism.

Melanin, as a substance possessing semiconductor properties, has been known since 1974, when McGinnes *et al.* [1] established that this compound exhibits the effect of switching from weakly to highly conducting state under the action of relatively small electric fields. Recently, Rosei *et al.* [2] studied the spectral and photoelectric properties of synthetic melanin and proposed a mechanism explaining the photo-production of charge carriers.

The purpose of our study was to measure the absorption spectra of natural melanin, the effect of UV irradiation on the samples, and the photoluminescence at room and low (liquid helium) temperatures.

The experiments were performed with melanin extracted from raw plant material. In respect to the structure, the extracted substance was close to synthetic melanin based on a 5,6-indolequinone monomer [2], as confirmed by the results of chromatographic measurements and elemental analyses. The sample films were prepared by applying a melanin solution (in alcohol possessing a complicated molecular structure) onto quartz substrates at room temperature.

The absorption spectrum of melanin measured in the visible spectral range (Fig. 1, curve 1) exhibit a monotonic decrease from 375 to 800 nm. This shape of the absorption spectrum was explained [2] as resulting from a disordered structure of the melanin film composed of elementary nanodimensional two-dimensional

clusters packed into stacks. According to this model, the absorption spectrum of melanin is explained by the π - π^* electron transitions inside nanoclusters. The observed absorption spectrum is untypical of organic compounds, being closer in shape to the spectra of disordered amorphous inorganic semiconductors [3].

For comparison, Fig. 1 shows the absorption spectra of a melanin film irradiated for 1.5 h by nonfiltered polarized light of a mercury lamp (DRSh-250-2). The measurements were performed using a beam polarized in directions parallel (curve 2) and perpendicular (curve 3) to that of the irradiating light. As can be seen, the irradiation does not modify the character of the spectrum on the whole: there is only an insignificant change in the slope and a small (5–15%) decrease in the absorption coefficient in the region of 375–400 nm. The latter decrease depends on the polarization, being more pronounced for the spectrum measured using

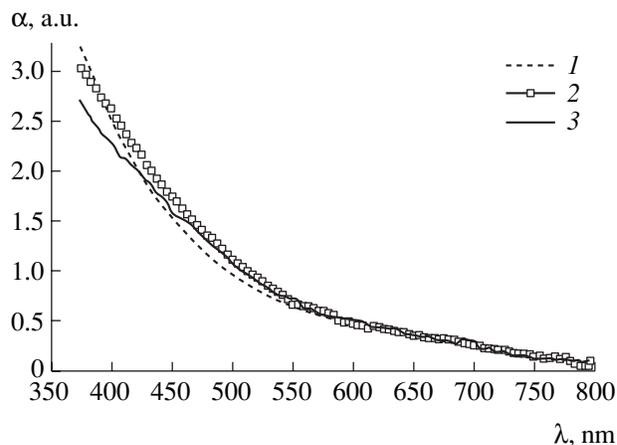


Fig. 1. The optical absorption spectra of (1) unirradiated and (2, 3) UV-irradiated melanin films measured using (2) parallel and (3) perpendicular polarization of the probing beam.

light polarized in the perpendicular direction. This result is additional evidence of the absence of linear structures typical of most polymers.

Using the measured absorption spectrum (Fig. 1, curve 1), we estimated the optical bandgap width E_g^{opt} of melanin. This was done using the Tautz law, according to which the plot of $(\alpha E)^{1/2}$ versus energy E for amorphous solids with three-dimensional electron states must be linear. By extrapolating this plot to the abscissa axis, it is possible to determine the E_g^{opt} value of such a disordered substance [3].

Since the melanin films studied also possessed a disordered structure, it was possible formally to employ the Tautz formula [2, 3]. However, the plots of $(\alpha E)^{1/2}$ versus energy E in our case (unlike that reported in [2]) were not strictly linear. To a first approximation, the experimental curve could be divided into two linear parts, the extrapolation of which yields $E_g^{opt} \sim 1.4$ and ~ 1 eV. Using an exponent of 0.3 instead of 0.5 (as was done, e.g., in [4]) provided a better linearization of the experimental data, in which case we obtained $E_g^{opt} = 1.2 \pm 0.2$ eV. This change in the exponent was justified [4] as resulting from fluctuations (scatter) in the dimensions of nanoparticles. It should also be noted that, as was correctly indicated, e.g., in [5], the estimated energy corresponds, strictly speaking, to a minimum energy of the $\pi-\pi^*$ electron transition ($\pi-\pi^*$ gap) [5].

According to the most commonly accepted model [6], the dependence of the change in the optical bandgap width ($\pi-\pi^*$ gap) on the size of nanoparticles (conjugation length) is described by the relation $\Delta E_g^{opt} \sim C/d^2$, where C is a constant and d is the particle diameter. Using this relation, it is possible to estimate the ratio of the size of nanoclusters corresponding to the two estimates of E_g^{opt} : $d_2/d_1 = (E_{g1}^{opt}/E_{g2}^{opt})^{0.5} = 0.85$. From this we may conclude that the films studied exhibit a bimodal distribution of nanocluster dimensions with two most probable values (conjugation lengths).

This conclusion is confirmed by the results of measurements of the photoluminescence (PL) spectra of melanin films at 5 and 300 K (the experimental procedure was described in detail elsewhere [7]). Figure 2 presents the spectra of stationary and time-resolved PL (the latter measured at a nanosecond delay time). As can be seen, the room-temperature stationary PL spectrum consists of two intense narrow bands peaking at 375 and 440 nm and a broad structureless band with a maximum at about 660 nm (Fig. 2, curve 1). In the time-resolved PL spectrum (measured at a nanosecond resolution), the intensity of the narrow bands somewhat decreases and the broad band disappears (Fig. 2, curve 2). The spectra of stationary and time-resolved PL measured at liquid-helium temperature differ rather

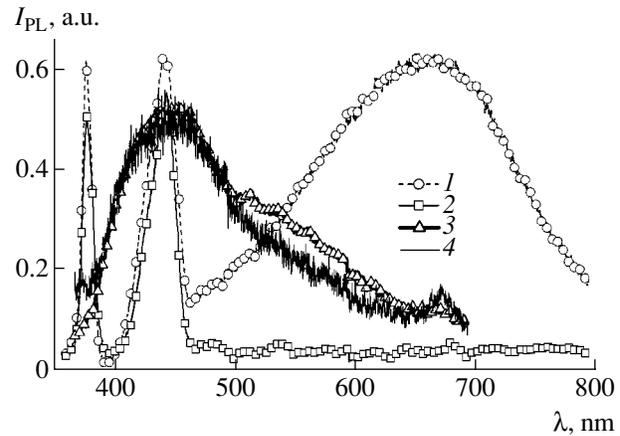


Fig. 2. The spectra of (1, 3) stationary and (2, 4) time-resolved ($t_d = 3$ ns) photoluminescence of a melanin film measured at (1, 2) 300 K and (3, 4) 5 K.

slightly from each other (Fig. 2, curves 3, 4). In comparison to the corresponding room-temperature spectra, the intensity of the band at 375 nm drops to almost zero and the band at 440 nm exhibits a significant broadening. The band at 660 nm is absent from both PL spectra measured at 5 K.

The results of our PL measurements can be interpreted as follows. The narrow emission bands correspond to the excitation of nanoclusters of the two most probable dimensions and represent the electron transitions inside these clusters (between their fragments). For this reason, these bands are observed in both stationary and time-resolved PL spectra. Note that the ratio of the energies of these bands (0.85) coincides with the estimate of the ratio of the most probable dimensions of nanoclusters. The broad structureless band, manifested only in the room-temperature stationary PL spectrum, probably reflects the interaction of structural elements (clusters) with each other and is due to the excimer radiation. A similar pattern is observed, for example, in many conjugated polymers where the PL spectra contain narrow bands caused by emission from conjugated fragments and broad structureless bands with rather large lifetimes ($>1 \mu\text{s}$) caused by excimer (dimer) radiation [8].

At low temperatures, one (less stable) type of nanocluster is probably subject to irreversible breakage, which accounts for the disappearance of the emission band at 375 nm. A change in the structure of melanin, manifested in an increase in the homogeneity of the film, can be observed using an optical microscope.

Thus, the results of investigation of the absorption and photoluminescence spectra of melanin show that a film of this natural biomolecular semiconductor is composed of stacked nanoclusters (manifested by the presence of excimer radiation). This nanocluster structure with two most probable cluster types probably deter-