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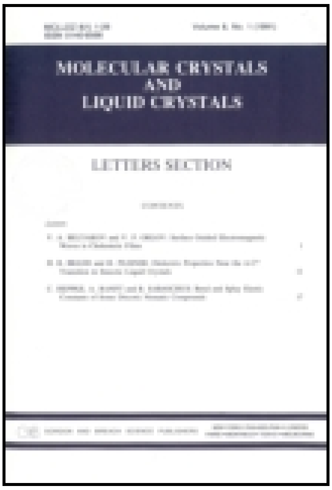

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Photovoltaic Properties of Fungal Melanin

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Photovoltaic Properties of Fungal Melanin

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The films of fungal melanin (FM) were fabricated from solution, and also optical and photovoltaic properties of the films and heterostructures with other semiconductors were studied. Color and absorption spectra of studied FM were like in eumelanin. Photovoltage of ITO/FM structures under illumination of the free surface side is 2–3 orders of magnitude lower than in the films of phthalocyanines and polyacenes. The photovoltage of double layer heterostructures of FM with C_{60}, $SnCl_2$ phthalocyanine, sulfonamide zinc phthalocyanine, lead phthalocyanine, pentacene is lower than one in the ITO/FM structures under illumination through the free surface and in organic semiconductor films.

Keywords Fungal melanin; optical and photovoltaic properties; films; heterostructures

1. Introduction

In recent years, properties of solutions and films of various melanins are widely studied due to their growing medical application [1]. However, the published data on the photovoltaic properties of the melanin films are very scarce [2–4]. The study of dye-sensitized solar cells (DSSC or Grätzel cells) made up of chemically synthesized melanin, eumelanin, revealed its poor performance yielding up to 0.34% of light to electricity efficiency [3]. Moreover, the feasibility to prepare solar cells based on natural melanin contained in the hair has been quite ambiguously discussed for a while in scientific community [4]. Thus, an issue about the prospects of using melanin in photovoltaics is still open. Therefore, we performed preliminary studies of optical and photovoltaic properties of the films of FM fabricated by drop-cast from water solution on quartz and indium tin oxide (ITO) coated glass substrates.

2. Experimental

Powder of studied FM, which is successfully used for the manufacture of medicines, was extracted from basidial fungi, and then further purified by Prof. L.F. Gorovyi (Institute of Cell Biology and Genetic Engineering, National Academy of Sciences of Ukraine) [1]. Color and shape of absorption spectra in the visible spectral range for studied FM is close to eumelanin. Thus, to characterize FM we have analyzed absorption and photoluminescence of the drop-cast films and aqueous solutions of FM before and after additional purification, comparing the results with the properties of eumelanin studied in Ref. 5.

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Table 1. Data of elemental analysis of unpurified and purified FM, and comparison with eumelanin

Material	N, %	H, %	C, %	X, %
unpurified FM	0.45	1.85	20.3	77.4
purified FM	2.6	3.7	38.4	55.3
eumelanin ($N_{10}H_{46}C_{74}O_{36}$) [8]	8.5	2.8	53.6	35.1

Melanins, including eumelanin, are insoluble in water, acids, organic solvents, but are well soluble in alkalis and precipitate in acidified solutions [6]. A discriminative feature of studied FM is good solubility in distilled water. In other words, this feature may be due to a presence of impurities or specific substitutions in FM. The impurities being most likely present in FM are amino acid of tyrosine, which is a building unit in melanin polymerization, glucan and chitin - biopolymers, which are the main components of the fungus [7].

The concentrations of the impurities in the studied FM are unknown. To monitor the effectiveness of the additional purification (hereafter, samples before and after purification are named unpurified and purified, respectively) an elemental analysis of FM powder was carried out at the Carbo-Erba analyzer (accuracy of 0.2% by weight). Data of the content of N, H, C and other elements (X) elements were summarized in the Table 1 and compared with data for eumelanin.

According to the elemental analysis, the content of N, H and C in unpurified FM was 0.45, 1.85 and 20.3%, respectively, and after purification it was 2.6, 3.7 and 38.4%, respectively. This way, the content of N, H and C in purified FM is higher, same time being much lower than in eumelanin (*Sepia* melanin), $N_{10}H_{46}C_{74}O_{36}$, has (8.5, 2.8, and 53.6%, respectively) [8]. Thus, the purification significantly reduced the concentration of both additives with low content of nitrogen and oxidation products (X). The total amount of impurities extracted in refining process reaches approx. 20% (see ΔX. in Table 1).

Films of FM were fabricated by drop-casting 1% aqueous solution of FM on quartz substrates covered with or without a conductive layer of ITO. The absorption spectra of the studied solutions and films were measured with Shimadzu UV2450 UV-VIS spectrophotometer, and photoluminescence spectra measurements were carried out with a special complex described in Ref. [9]. Photovoltage was measured by the static capacitor technique described in Refs. [10, 11] using modulated illumination from serial light-emitting diods (LEDs), intensity of which is much higher than the output of the halogen lamp passed through monochromator.

3. Results and Discussion

3.1 Optical Properties of FM

The measured absorption spectra for the films and aqueous solution of FM appeared to be similar to the eumelanin spectra, i.e. nonselective in the range of 400-800 nm, and hence can be fitted by straight line in semi-logarithmic scale (Fig. 1). However, a slope of the line for solution of FM is higher (1.6–1.8 times) than that for eumelanin solution. The slope of unpurified and purified FM is the same (Figure 1, curves 1 and 2). This means that the impurities and oxidation products do not dissolve in water or absorb in more short-wavelength range. The difference in the slope of eumelanin and FM is not evident, although

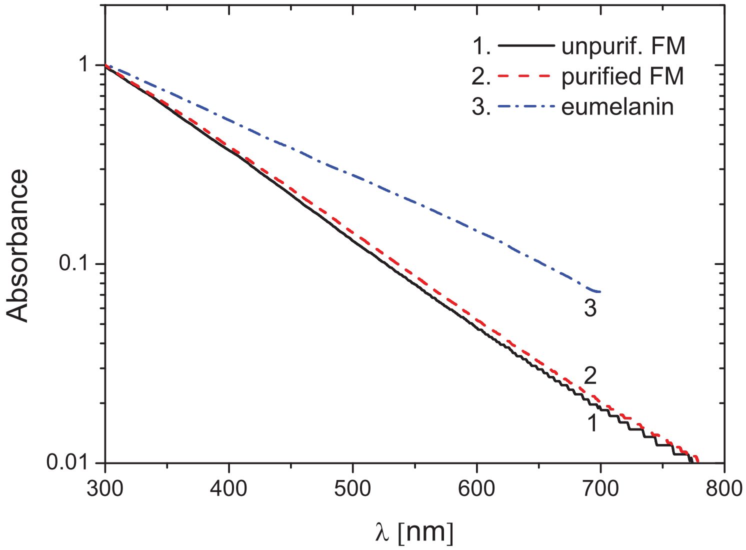

Figure 1. The absorption spectra of unpurified (1) and purified (2) aqueous solutions of FM and eumelanin [5] (3).

it is likely to be a reason of various solvents or different experimental setups, as well as a presence of various impurities in the solutions.

The nonselectivity of absorption spectra of melanins is not a property of individual units of melanin macromolecules, which is clearly seen from comparison of the excitation and absorption spectra (Fig. 2) of well-purified eumelanin [5]. The difference between

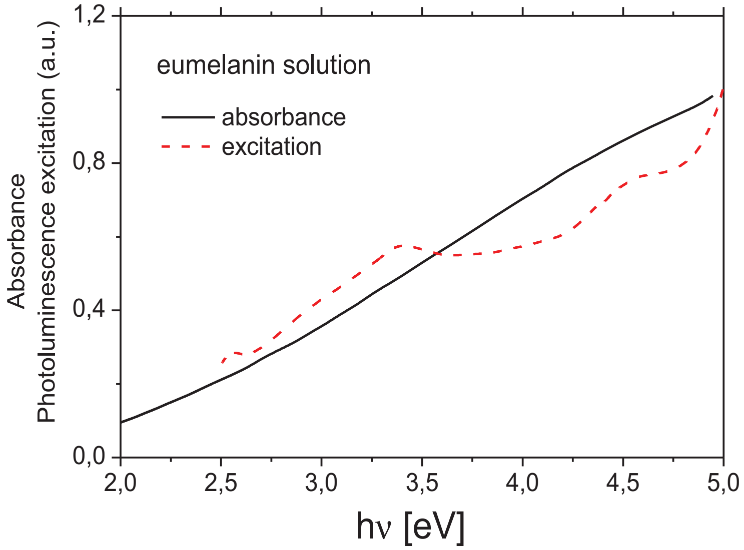

Figure 2. The absorption (solid) and photoluminescence excitation (dashed) spectra of aqueous solution of eumelanin [5].

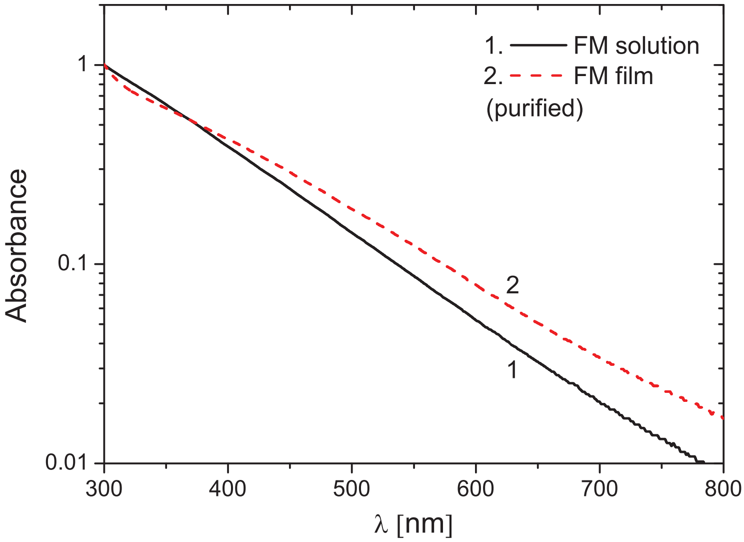

Figure 3. The absorption spectra of aqueous solution (1) and film (2) of purified FM.

the spectra in Fig. 2 is due to the fact that no scattered light generates a luminescence. Luminescence occurs only when the molecules absorb the light.

Generally, the nonselectivity of absorption spectra is due to the chemical heterogeneity in bonding of melanin units into macromolecules (*chemical disorder model* [5]), absorbance of impurities and complexation of melanin with impurities, as well as the contribution of luminescence and light scattering. All factors differently depend on the wavelength that leads to nonselectivity of absorption spectra, and contributes to the difference in slopes of absorption spectra of solutions and films of FM (Fig. 3).

Figure 3 shows that the studied FM films have additional absorption in comparison with the solutions, and the intensity of the additional absorbance increase with longer wavelength, λ, of the spectra. Light scattering should increase with decreasing wavelength. Therefore, it is clear that the growth of the additional absorption with increasing λ can be due to a formation of impurity complexes with FM in the film fabrication. To confirm this, we measured the photoluminescence spectra of solutions of purified and unpurified FM (Fig. 4) as well as the films (Fig. 5).

Figure 4 shows that the photoluminescence spectrum of FM in solution consists of asymmetric band with a maximum at 450–470 nm (Fig. 4, curve 1). Asymmetry of the band evidences a presence of at least two simple bands - long-wavelength ($\lambda > 460$ nm) and short-wavelength ($\lambda < 460$ nm) ones. Moreover, the intensity of long-wavelength band is a little bit higher in solution of purified FM (Fig. 4), and thus being well illustrated by the spectral dependence of the ratio of the spectra (Fig. 4, curve 3). This could be explained with formation of a small amount of the complexes of FM with water soluble impurities featured by a broad PL ratio band in the range of 550–650 nm. The increase in photoluminescence of purified FM in regard to unpurified one seemed to impede this explanation. However, it should be noted that in result of purification the concentration of impurities that do not interact with melanin, could decrease, but the concentration of melanin in the purified powder, and solution as well, is obviously higher, so that should lead to an increase in intensity of photoluminescence.

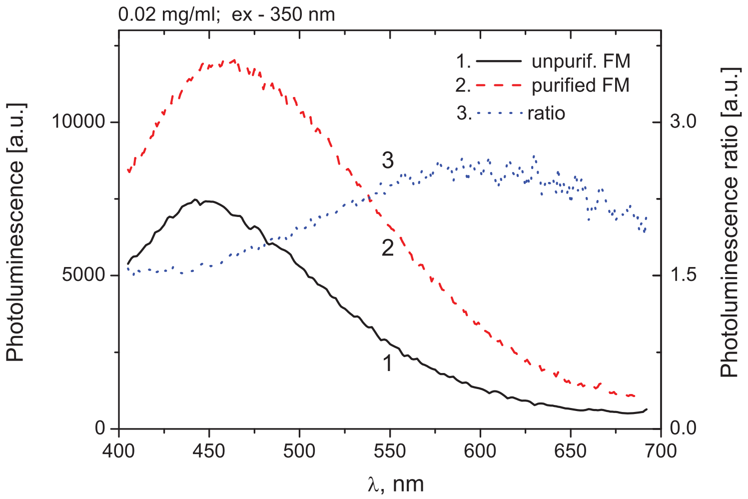

Figure 4. Photoluminescence spectra of aqueous solutions of unpurified (1) and purified (2) FM and the spectral dependence of its ratio (3).

A comparison of photoluminescence spectra of the film and solution of FM (Figure 5) shows that in the result of the film formation the intensity of the short-wavelength ($\lambda <$ 460 nm) component of the film spectrum with a maximum in the range of 420–470 nm is largely reduced. Thus, the long-wavelength component dominates in the film spectrum of photoluminescence having apparent maximum at 520 nm. In addition, the photoluminescence spectra of the films have weak spectral features in the 620–680 nm region, which do not appear in the solutions. These bendings are present in both purified and unpurified FM. Clearly, the probability of the formation of aggregates and complexes between various

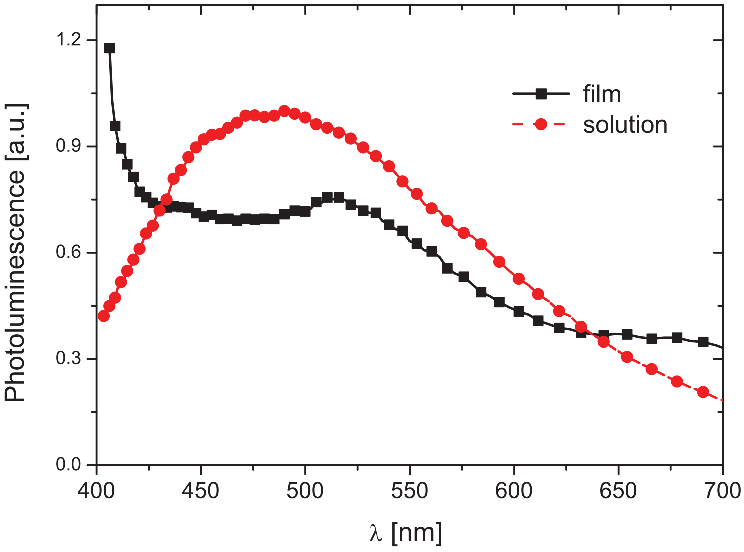

Figure 5. Photoluminescence spectra of the film (1) and aqueous solution (2) of FM.

Table 2. The photovoltages through free surface side illumination for unpurified (V_U) and purified (V_P) FM

Color of LED irradiation		IR	Red	Green	Blue
Enery of LED maximum output, *hv*, eV		1.32	1.91	2.175	2.64
Power of LED irradiation, P, μW		5.08	0.3	0.466	1.86
Material	parameters				
Unpurified FM	V_U, μV	10	13	20	22
	V_P/P, V/W	2	43	43	12
Purified FM	V_P, μV	8	11	35	25
Purification effect	$(V_P-V_U)/V_U \times 100\%$	−20%	−15%	+75%	+14%

components is higher for films than that in solution due to reduced distance between the molecules. Therefore, the photoluminescence features in the range of $\lambda > 600$ nm can be explained by the formation of complexes of melanin with water-soluble impurities, since the photoluminescence in the region of $\lambda > 600$ nm is not characteristic for the films and solutions of melanin [5, 12].

3.2 Photovoltage of ITO/FM Structures

Photovoltage of FM films (ITO/FM structures) under illumination through free surface side by LEDs irradiation is 2–3 orders of magnitude lower than in the films of phthalocyanines ($SnCl_2$ phthalocyanine, sulfonamide zinc phthalocyanine, lead phthalocyanine) and polyacenes (pentacene being one of the most photosensitive organic semiconductors). Illumination of the structures through ITO electrode results the photovoltage one order of magnitude lower than one under illumination through free surface side. The most likely reason for the difference in the photovoltages is heterogeneity of the FM films by the thickness, so thus, the ITO/FM interface featured with high rate of charge carrier recombination. Perhaps, this is due to a higher concentration of residual water at the interface of ITO/FM. The values of photovoltage under illumination through free surface side for unpurified and purified FM are summarized in Table 2.

Table 2 shows that the photovoltage increases in result of purification in the visible region, with the highest yield in 75% for green LED (with $\lambda = 570$ nm / 2.175 eV). In the long-wavelength (red and near-infrared) region ($\lambda > 650$ nm), the photovoltage decreased by 15–20%. The photovoltage is one order of magnitude higher under illumination through free surface side than that under illumination through the ITO-electrode regardless of LED wavelength. Thereafter, the photovoltage under illumination through the ITO-electrode is in the range of the precision of measurement, i.e. noise level. This way, in Table 2 and 3, one presents data for free surface side irradiation, namely, the absolute values of photovoltage, V, the photosensitivity determined as the photovoltage vs incident radiation intensity, $S = V/P$, and the photosensitivity normalized on absorbed light, S/D, where D – optical density of FM films at the illumination wavelength.

The Table 3 shows that the photosensitivity parameters strongly depend on the wavelength of LEDs radiation and have a maximum for greed LED (2.175 eV / 570 nm). It should be noted that the maximum value of photosensitivity is almost the same as the maximum for the ratio of the photoluminescence spectra of purified and unpurified FM

Table 3. The photovoltage, V, the photosensitivity, S = V/P, and the photosensitivity normalized on absorbed light, S/D, for purified FM

Color of LED irradiation	IR	Red	Green	Blue
Enery of LED maximum output, *hν*, eV	1.32	1.91	2.175	2.64
Power of LED irradiation, P, μW	5.08	0.3	0.466	1.86
V_P, μV	8	11	35	25
S = V_P/P, V/W	1.57	36.67	75.11	13.44
D	—	0.614	0.8	1.307
S/D	—	59.72	93.89	10.28

solutions, which was explained by the formation of complexes, i.e. it is not connected with melanin monomers.

3.3 Photovoltaic Properties of Heterostructures Made Up of FM

In double layer heterostructures of FM with photosensitive organic semiconductor films, the photovoltage is lower than that in the structures ITO/FM under illumination through free surface side and 2–3 orders of magnitude lower than that in photosensitive organic semiconductor films (C_{60}, lead phthalocyanine, $SnCl_2$ phthalocyanine, sulfonamide zinc phthalocyanine, pentacene). The most likely components of an aqueous solution of FM dope the films of organic semiconductors reducing photosensitivity and forming a large number of centers of charge carriers recombination at the interface. The only studied heterostructures with layers of CuI and a co-polymer, 3-iodium-9-vinylcarbazol with octylmetacrylate (I-VC:OMA), have slight increase in the photovoltage (2 times). An average growth of the photovoltage in the heterostructures of CuI is 2.14, mainly in the long-wavelength region, and the maximum increase was observed for the red LED (650 nm / 1.91 eV).

Thus, the FM films without proper doping or composite formation have very low prospects for the development of solar cells due to their low photosensitivity, weak absorption in the region of intense sunlight irradiation, and problems to form heterostructures with significant built-in electrical field at the interface.

4. Conclusions

For the first time, the optical spectral properties of aqueous solutions and films of fungal melanin were studied paying special attention on a purification of the material. It is shown that in the purification of the melanin results in a decrease of the concentration of biological contaminants with low nitrogen content and oxidation products. In the photoluminescence spectra of the films, bands with maxima were observed in the range of 420–470 nm, 520 nm and 620–680 nm, whereas the band at $\lambda > 600$ nm may be due to the formation of complexes of melanin molecules with water-soluble impurities. The study of photovoltaic properties of the films of fungal melanins has been shown that the maximum photosensitivity observed in the range of absorption of above complexes that can be used to develop a photosensitive thin film structures based on melanin.

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