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Optical properties of pure synthetic melanin and melanin doped with Iodine and Sodium- borohydride

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ABSTRACT

This research is focuses on the effect of doping with Iodine (I_2) and Sodium-borohydride ($NaBH_4$) on optical properties of melanin pigment. Thin films of pure melanin and melanin doped with ((I_2) and ($NaBH_4$)) have been prepared by spray on evaporator method. The optical properties were characterized by 300 – 800 nm wavelength range measurement. The optical characteristics indicate that the melanin doped with ($NaBH_4$) exhibited the lower absorbance, broaden band gap and high n values, where as the melanin doped with (I_2) exhibited the higher absorbance, narrowed band gap and high k values. The energy band-gap of pure melanin was found to be 2.6 eV.

Keyword: Melanin thin films, Optical properties, Iodine, Sodium- borohydride.

INTRODUCTION

Naturally occurred melanins are a class of pigments, ranging in color from the yellow and red-brown to the brown and black responsible for coloration in our hair, skin and eyes [1-6]. They are a class of bio macromolecules (biopolymer) found throughout nature and are thought to be macromolecular semiconductor [1, 6, and 7]. Melanins basic types are eumelanin, the pre- dominants form in humans, composed of 5-6-dihydroxyindoe (DHI) and 5-6-dihydroxindol-2-carboxylic acid (DHICA) and pheomelanin composed of bensothiazines intermediates. Melanin is synthesized in specialized cells (the melanocytes) in the body by the action of the enzyme tyrosine. Synthetic melanin is prepared by the oxidation of tyrosine with Hydrogen peroxide [3, 8]. Melanin occurs in the form of extremely dense ellipsoidal granules 0.3μ by 0.7μ called melanosoms. They are broad band UV and visible light absorber that make them play a photoprotective rule as skin protector [6-11]. Melanins are chemically and photochemically very stable, virtually insoluble in most common solvents, and can effectively turn biologically harmful photons into harmless heat [12]. Recently the unusual set of physicochemical properties of synthetic eumelanins biopolymer has been proposed for optoelectronic and photovoltaic applications [13, 14]. This paper is devoted to study of the changes of optical properties of synthetic melanin, due to doping with Iodine (I_2) and sodium-borohydride ($NaBH_4$).

MATERIALS AND METHODS

EXPRIMENTAL PROCEDURE:

Pure melanin powders (sigma Aldrich M8631) (0.01% mol, 0.01 gm) was dissolved in 25 ml dimethylsulfoxide (DMSO), the solution was filtered by filter paper, and used for the preparation of pure melanin thin films. The melanin solution were deposited on a thoroughly cleaned glass substrates of dimensions of 27 mm, 25 mm and 1mm, to obtain thin films, by spray on evaporator method[15,16]. The evaporator temperature was taken to be 100 ^{o}C to ensure the solvent evaporation. Samples thickness (d) were calculated using the relation, (d $=M_2$ - $M_1/S\rho$) where, M_1 and, M_2 is the mass of sample glass substrate before and after deposition respectively, S thin film area and, ρ is the density of the material[17]. The same procedure was used to prepare 1wt% and wt5% Iodine (I_2) and 1wt% and 5wt% Sodiumborohydride ($NaBH_4$) doped melanin thin films. The electronic microscopy observations of the obtained pure and doped melanin thin films showe uniformity and cracks or voids free (see Fig. 1).

Pure and doped samples thicknesses are depicted in table (1). The optical absorbance versus wave length traces of all the films were recorded in 300 – 800 nm wavelength range using a double beam spectrophotometer (CE-7200).

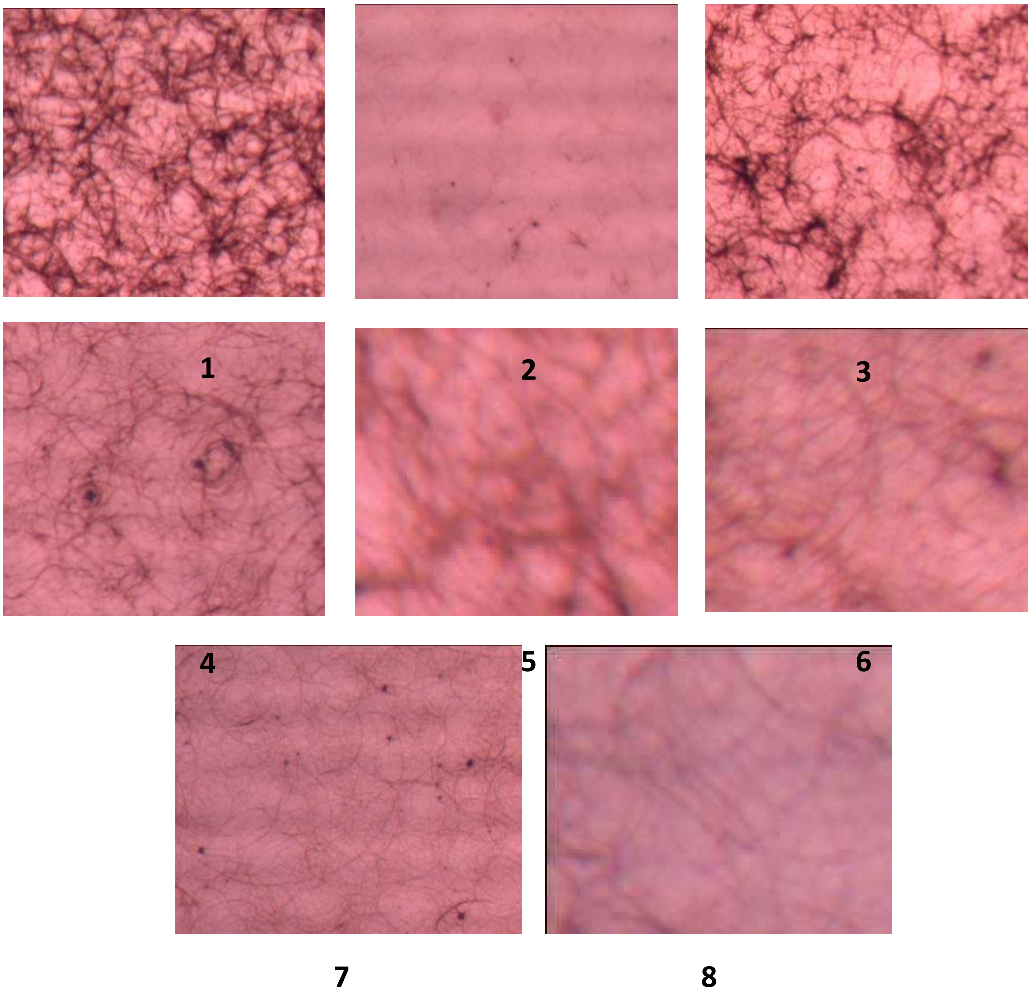

Figure 1: Images of pure and doped melanin thin films. (1-4)different thickness pure melanin thin films (5-8) 1wt% and 5wt% Iodine (I_2) and 1wt% and 5wt% Sodium-borohydride ($NaBH_4$) doped melanin thin films respectively.

Table 1Show pure and doped melanin thin films thicknesses

Thin film No.	Doping material	Doping (wt%) concentration	d (nm)
1	-	0	221
2	-	0	126
3	-	0	97
4	-	0	97
5	I_2	1%	95
6	I_2	5%	88
7	$NaBH_4$	1%	100
8	$NaBH_4$	5%	96

RESULTS AND DISCUSSION

Fig.2 shows the absorbance spectra of pure and doped melanin thin films. The pure melanin exhibits a broadband absorption spectrum with low absorbance (high transparency) of 06% - 26% between visible wavelengths of 450 nm – 800 nm. Low absorbency material is favorable for electronic devices such as solar cells. Higher absorbance at higher energies may give high protection against the most damaging high energy photons to the humans. Melanin doped with 1%wt Iodine shows higher absorbance spectrum.

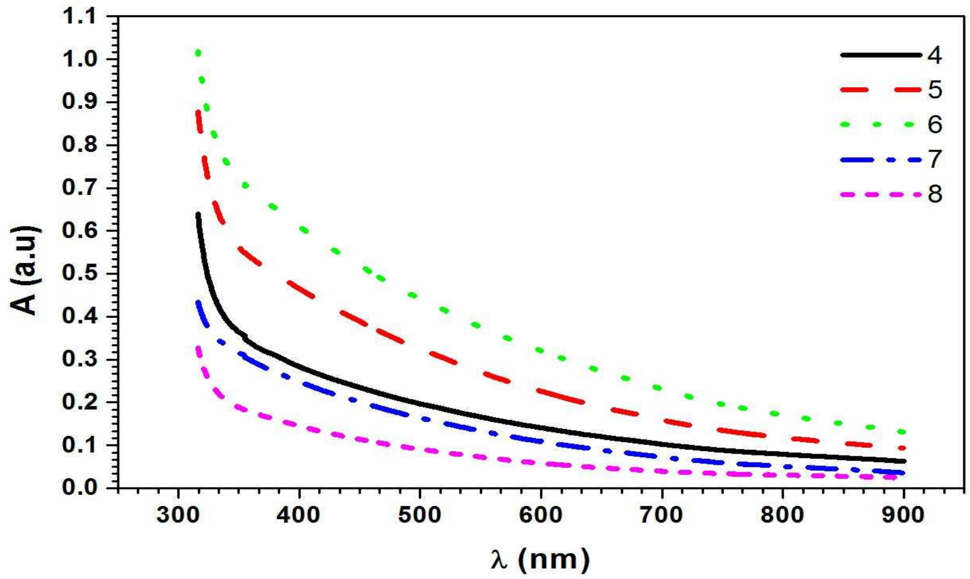

Figure 2: The absorbance spectra of pure and doped melanin thin films.

The absorption coefficient, α was calculated according to Beer-Lambert's law: ($\alpha = 2.303A/d$) where, A is the absorbance[18]. Fig. 3 shows the absorption coefficient spectra of melanins pure and doped thin films. It is obvious that spectra of all films exhibit low absorption in the visible and NIR region but high absorbance in the UV range. High absorption characteristics in the UV range are due to melanin wide band gap properties.

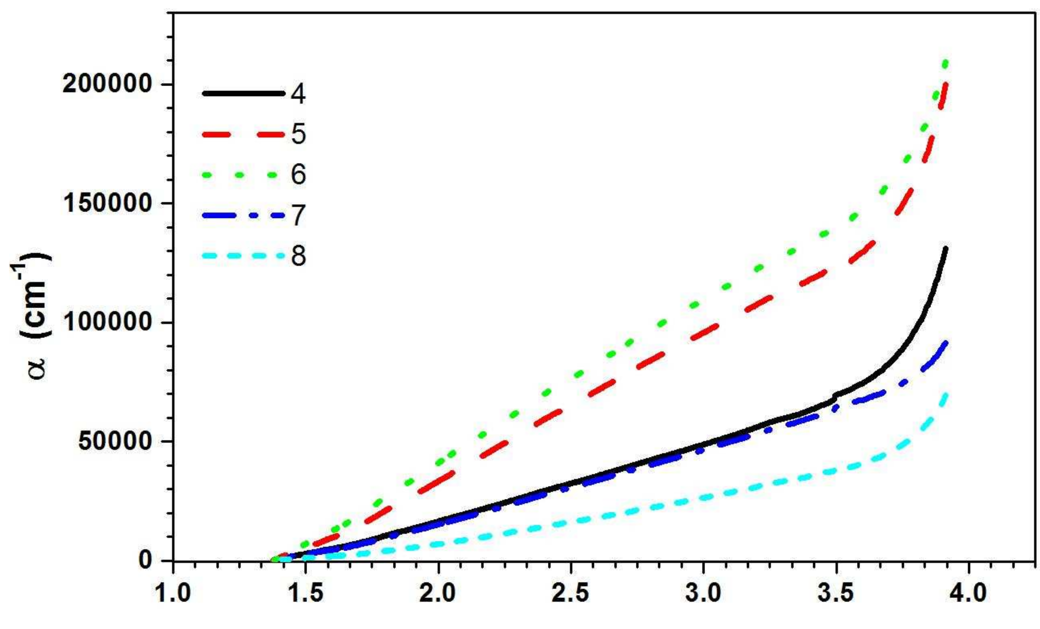

Figure 3: Absorption coefficient as a function of the energy of the incident photons for the samples.

The band-gap energy E_g which is associated with HOMO to LUMO electron transitions between the π and π*molecular orbitals[19], were estimated using Tauc's approach $\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$ of direct band-gap energy (where, $h\upsilon$ is the incident photon energy) by extrapolating the linear curve to the photon energy axis, we found that the band-gap energies of pure melanin as a function of thin films thickness are ~2.6 eV (Fig.4) which were close to the reported values of synthetic melanins [20-22].

The estimated energy gaps of pure and doped melanin were shown in Fig.5. and Table.1. The increase or decrease of the energy gap due to doping may be attributed to the amount of disorder in the material which probably plays an important role in the optical band gap [23], since the dopant deteriorate the structural properties, which in turn give rise to defect states and thus induce changes of absorption edge.

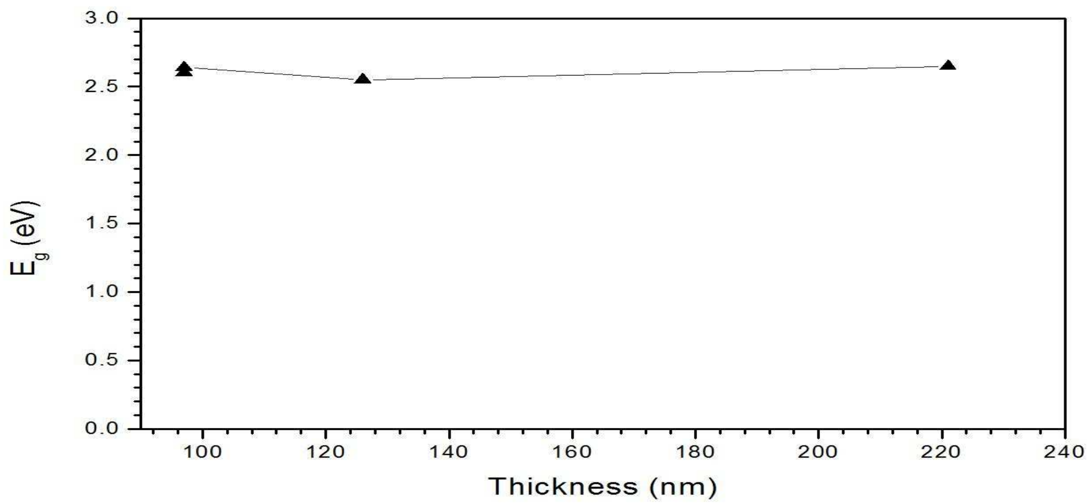

Figure 4: The optical band gap of pure melanin as a function of thin films thickness

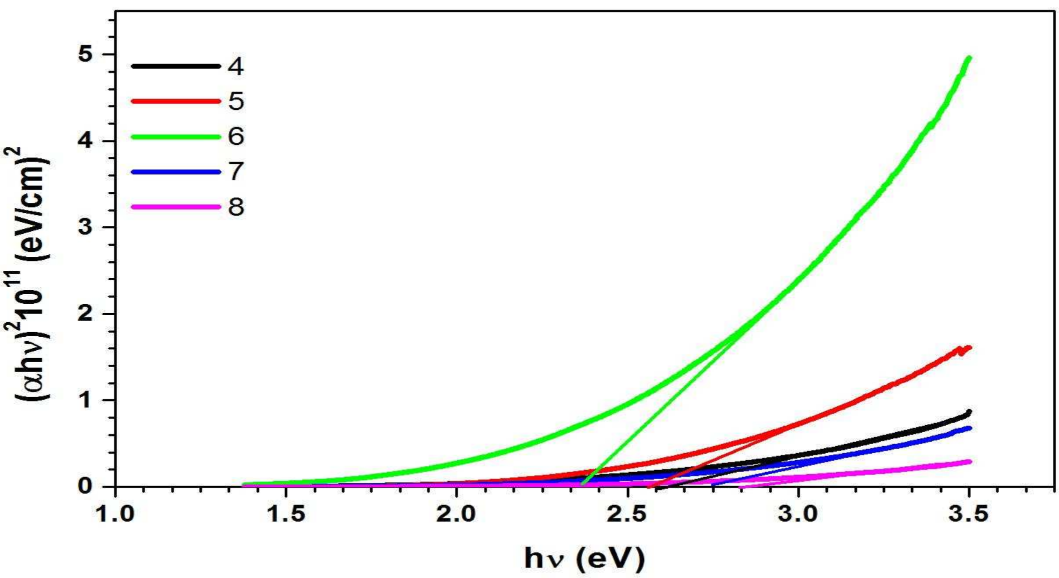

Figure 5: Optical band gap estimation of pure and doped melanin with different wt% (I_2) and $NaBH_4$ thin films using Tauc's plot $(\alpha h\upsilon)^2$ versus photon energy.

Table 2 Optical band gaps of pure and doped melanin with different wt% (I_2) and $NaBH_4$ thin films.

Sample	Dopant wt%	Energy gap Eg (eV)
4	0	2.60
5	1% (I_2)	2.55
6	5%(I2)	2.35
7	1% ($NaBH_4$)	2.75
8	5% ($NaBH_4$)	2.85

The extinction coefficient (k) and refractive index (n) were calculated according to the relations ($k=\alpha\lambda/4\pi$) and ($n=1+R^{1/2}/1-R^{1/2}$) respectively[24-25]. Extinction coefficient (k) as a function of incident photon energy is depicted in Fid.6. It is clear that k values for pure melanin are large for high-energy incident photons (UV) . This means that the high-energy photons have been highly attenuated [23] reflecting the photo-protective behavior of melanin against harmful solar light. High k values due Iodine doping may be related to high photogeneration (E_g becomes smaller) and other mechanisms such as access (phonon generation, free carriers absorption and scattering). It is obvious that doping with 1%wt ($NaBH_4$) has insignificant effect on k values, whereas 5%wt ($NaBH_4$) reduce k values as a consequence of the increase in band gap energy.

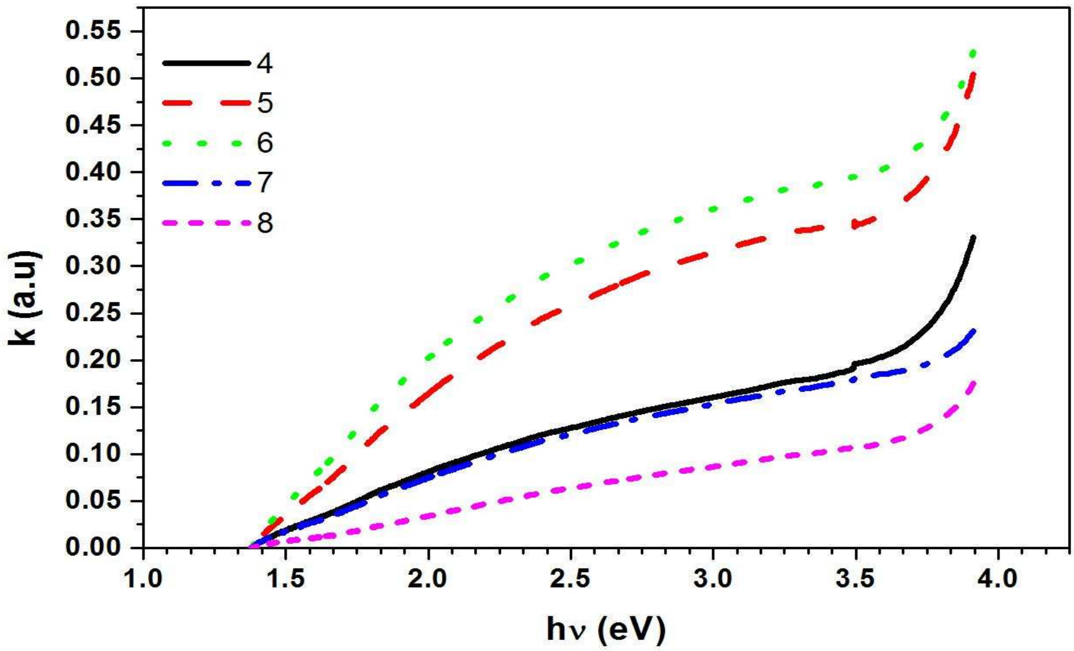

Figure 6: The extinction coefficient versus the energy of the incident photons for pure and doped melanin with different wt% (I_2) and $NaBH_4$ thin films.

The refractive indices of pure and doped melanin with different wt% (I_2) and ($NaBH_4$) thin films are depicted in Fig.7. It can be see that refractive indices of all thin films depends on the wavelength of light, and increase as wavelength increase in the range studied. It is also seen that doping with Iodine make the refractive index smaller and nearly wavelength (incident photon energy) independent.

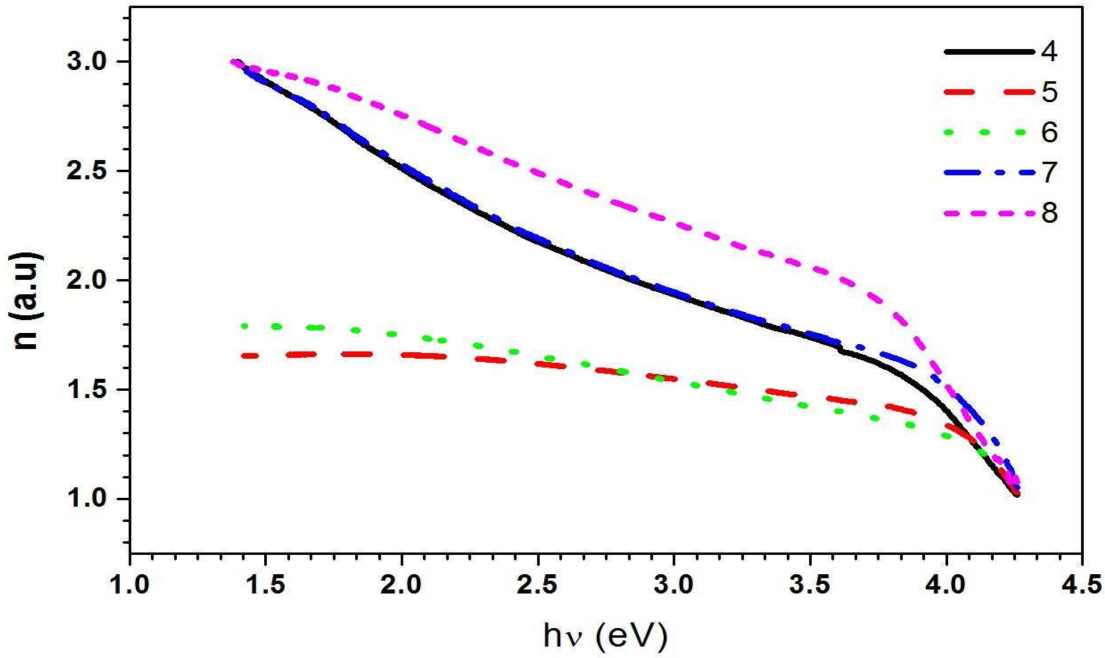

Figure 7: Refractive index as a function of the energy of the incident photons for the samples.

CONCLUSION

The absorption in eumelanin is broad and extending from the UV to the near-IR. The pure melanin has energy band gab of about 2.6 eV. Doping melanin with ($NaBH_4$) broaden the band gap and k values decrease , where as doping with Iodine narrowed the band gab and n values decrease

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