

Electrochemical Synthesis of Melanin Thin Films: Evolution of Structural and Optical Properties

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Abstract: *In the present work, melanin thin films were grown directly on ITO substrates by using simple electrochemical synthesis method. Formation of melanin films has been confirmed by low angle XRD, Raman spectroscopy and FTIR spectroscopy. Structural and optical properties of melanin films were carefully and systematically studied as a function of deposition time. The results obtained from low angle XRD analysis support the nano-aggregate model of melanin. UV-Visible spectroscopy analysis revealed that the melanin thin films have the absorption spectra similar to that of amorphous and disordered semiconductors. The SE) images show the uniform growth of melanin and full coverage of substrate with controllable thickness. The FTIR spectroscopy suggests the presence of different vibrational modes of melanin over the entire range of deposition time studied while Raman spectroscopy analysis shows the presence of vibrational modes of different functional group of melanin structure. Furthermore, investigation of the Raman and FTIR spectroscopy also shows that melanin thin films have biopolymer like structure and behave similar to the amorphous semiconductor. The ease of deposition of melanin thin films provides a new insight for potential applications in organic electronic devices.*

Keywords: *Melanin Thin Films, Low Angle XRD, Raman Spectroscopy, FTIR Spectroscopy, Scanning Electron Microscopy.*

1. INTRODUCTION

Melanin is a class of bio-functional macromolecule which is classified into Eumelanin and Pheomelanin. Eumelanin is a black brown nitrogen containing pigment of animal origin. Eumelanin is particularly found in black hair, skin, inner ear and in retina of eyes. Pheomelanin is a yellow-reddish color alkali soluble material containing nitrogen, sulphur polymer and found in red hair and red feathers. Unlike eumelanin, pheomelanin consist of mainly of benzothizine units with some of those degraded in benzothizoles. In recent years, melanin has drawn the attention of scientists due to its interesting physical and chemical properties such as photo-activity, electrochemical response, and amorphous semiconductor behavior. The combination of optical and electrical properties in melanin has made it a potential material for organic solar cells and other novel electronic devices. For example, melanin exhibits a broad band absorption which may be suitable for their use as sensitizers in photovoltaic devices. Good electron conductivity, appreciable ionic conductivity, and memory switching make them promising active components in organic electronic devices of low environmental impact [1-3]. Very recently, interest in melanin implementations for bio-devices as organic sensors, bio-electronics components [4, 5], and bio-materials [6] were renewed by the achievement of device quality films deposition [7].

There are various methods have been employed for the synthesis of synthetic melanin. These includes electro-spray deposition (ESD) [8], spin coating [7], electro-chemical deposition [9], auto-oxidation method [10], matrix assisted pulsed laser evaporation (MAPLE) method [11], spray pyrolysis [12], chemical bath deposition (CBD) [13], cold pressing [14], evaporation [15], constant potential method [16] etc. Each method has its own advantages and limitations. The major obstacle in preparation of melanin thin film is that it is not easily solvable in usual standard solvents. It makes difficult the deposition of homogeneous films and their structural characterization. Structure and functional relation has not been established yet, due to the complexity of the system. Casting or spin-coating techniques are among the most commonly employed ones, but are not able to guarantee an overall homogeneity of the films, mainly due to the unavailability of easily evaporable solvents for melanin. Search for suitable solvent is going on and recently ammonia solution yielded homogenous film in microscale [7].

The electrochemical deposition is another method used for the synthesis of melanin thin films with its limitation on the film thickness and substrate preference [9, 17]. However, the capabilities of electrochemical deposition method for obtaining device quality melanin thin films have not been fully established and there is a lot of room for improvement. To best of our knowledge, till so far the electrochemical deposition method has not been extensively studied for the synthesis of melanin thin films and only few reports exist in the literature. With this motivation we initiated the detailed study of synthesis and characterization of melanin films by using electrochemical deposition method. An attempt has been made to study structural, morphological, and optical properties of the melanin films.

2. EXPERIMENTAL

2.1. Films Preparation

In the present study thin films of melanin were prepared by an electrochemical method using a three-electrode system viz; a counter electrode, a reference electrode and a working electrode. The potentiostat Adroit M-3015 (Range: 0-32 V) was used. Films were deposited on ITO substrate which acts as a working electrode. Graphite was a counter electrode. The distance between working electrode and counter electrode was kept 1 cm. Saturated calomel was used a reference electrode. The potential were kept constant whereas deposition time varied in steps of one hour. Synthetic melanin powder M8631-250 mg (Sigma-Aldrich) has been used directly without further purification. The melanin powder was dissolved in dimethyl sulfoxide and methanol solution (DMSO/CH₃OH = 1:20) of 0.2 mg/ml concentration. The ITO substrate were initially cleaned with soap solution and then with double distilled water and finally cleaned in acetone with ultrasonic bath for 10 minutes. The substrate was dried by nitrogen (N₂) gas. The above cleaning procedure gives good adhesion of the film to the substrate. The pH of the solution was kept 6.8. After synthesis, samples were rinsed extensively with double distilled water and then dried in ambient air.

2.2. Film Characterization

The FTIR spectra were recorded in transmission mode by using FTIR spectrophotometer (JASCO, 6100-type A) in the range of 400-4000 cm⁻¹. The absorbance was measured using a JASCO, V-670 UV-Visible spectrophotometer in the range of 300-1100 nm. Raman spectra were recorded using Raman spectroscopy (Jobin Yvon Horibra LABRAM-HR) in the range of 1000-1800 cm⁻¹. The spectrometer has backscattering geometry for detection of Raman spectrum with the resolution of 1 cm⁻¹. The excitation source was 632.8 nm line of He-Ne laser. The power of the Raman laser was kept less than 5 mW to avoid laser induced crystallization on the films. Low angle x-ray diffraction patterns were obtained by x-ray diffractometer (Bruker D8 Advance, Germany) using CuK α line ($\lambda = 1.54 \text{ \AA}$) at a grazing angle of 1^o. The average melanin grain size has been obtained from the classical Debye-Scherrer equation [18]. The scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6360A microscope with operating voltage 20 kV to study the surface morphology of the films.

3. RESULTS AND DISCUSSION

It has been observed that the synthetic melanin thin films prepared in our electrochemical set up show a uniform coverage of the substrate together with a good mechanical adhesion. This result agrees with the experiments carried out by *da Silva et al.* [15], who have demonstrated the strong improved adherence of synthetic melanin films based on Dimethyl sulfoxide (DMSO) solutions evaporated by casting to Si substrates.

3.1. Variation in Film Thickness

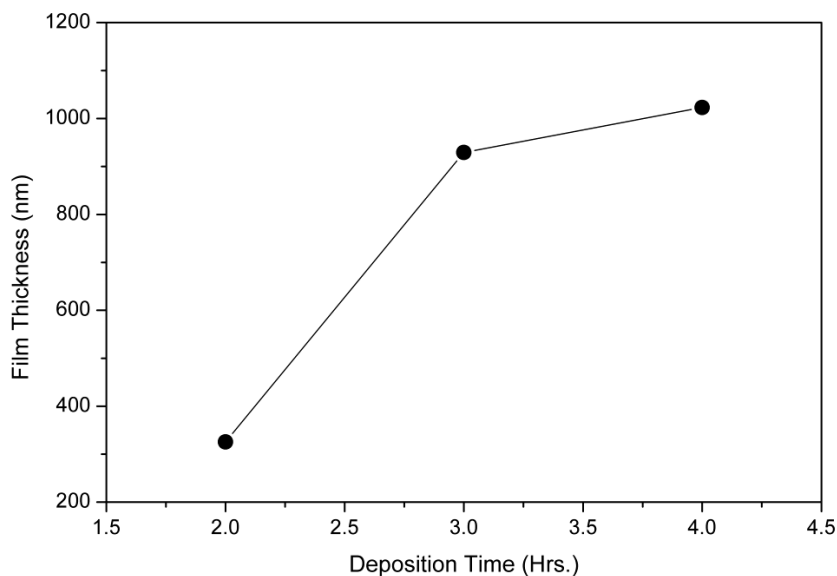


Fig 1. Variation of film thickness of the melanin film as a function of deposition time

The thickness of the melanin thin films was measured by an electro-mechanical contact Talystep surface profilometer (KLA-Tencor profiler). Fig. (1) shows the variation of thickness of the melanin thin films film as a function of deposition time.

As expected the thickness of the melanin film increases with increase in deposition time. It increases from 326 nm to 1023 nm when deposition time increased from 2 hrs to 4 hrs. As a result, the deposition rate increases from 2.72 nm/min to 4.26 nm/min when deposition time increased from 2 hrs to 4 hrs.

3.2. Low Angle X-ray Diffraction (XRD) Analysis

The formation of melanin films using electrochemical method is confirmed from the low angle x-ray diffraction analysis. The films deposited on ITO substrates were used for x-ray diffraction measurement. Fig. (2) display the low angle XRD pattern of the films deposited at various deposition time. The average grain size ($d_{x\text{-ray}}$) estimated using the Scherrer formula is also shown in the figure. As seen from the low angle XRD pattern, a shoulder centred at $2\theta \sim 21.4^\circ$ have been observed for all the synthesized films which are analogous to diffraction observed in natural melanin. The peak is due to x-ray diffraction from parallel planar layers of melanin. The peak position in the diffraction pattern give information about interlayer spacing d , according to the Bragg equation,

$$2d \sin\theta = n\lambda \quad 1$$

Where d is distance between the crystallographic planes, θ is the angle of diffraction, n is of the order of diffraction and λ is the wavelength of x-ray used. By considering the first order diffraction ($n = 1$) we obtain average inter-planer distance $d \sim 4.15 \text{ \AA}$ for synthesized melanin films which is slightly higher than the reported value for the melanin [19]. The increased value of inter-planer distance in the present study may be due to the presence of residual molecules between the parallel planar layers of melanin [14].

The average grain size ($d_{x\text{-ray}}$) estimated using the Debye-Scherrer formula are found to be 22.6 \AA , 31.1 \AA and 25.3 \AA for the films deposited at deposition time 2, 3 and 4 hrs respectively. These values support the nano-aggregate model of melanin suggested by *V. Capozzi et al.* [14].

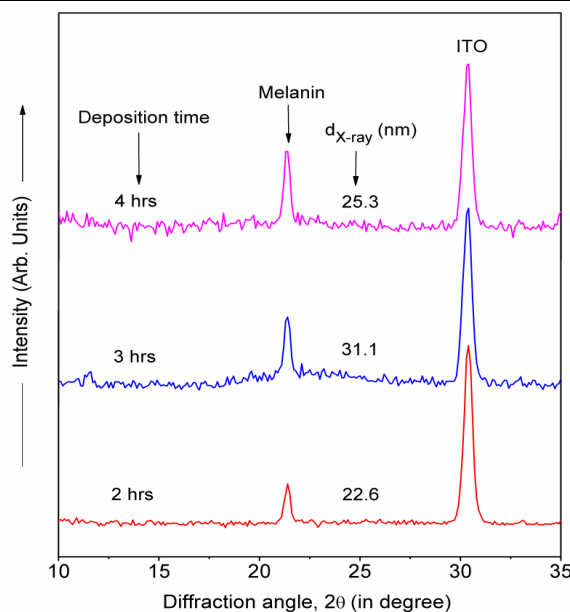


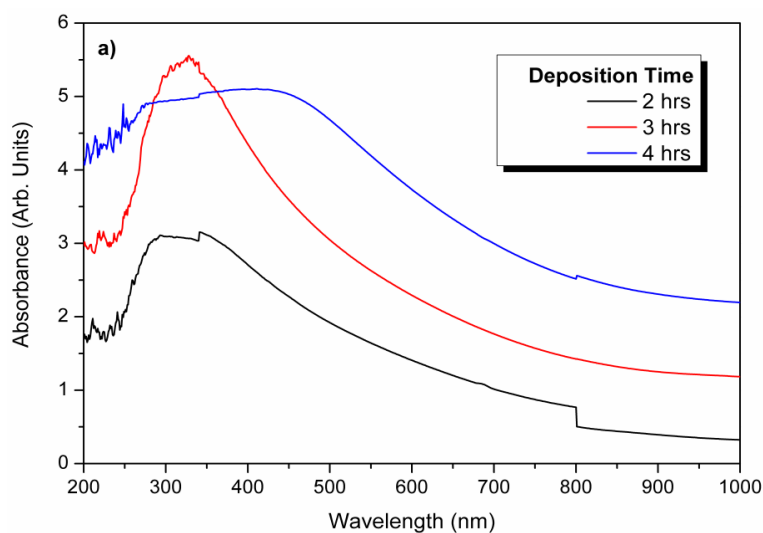
Fig 2. Low angle XRD pattern of melanin films deposited at different deposition time

3.3. UV-Visible Spectroscopy Analysis

Fig. 3(a) illustrates the UV-Visible absorption spectra of melanin thin films deposited at different deposition time using electrochemical deposition method. As seen from the figure the absorption increases exponentially towards the shorter wavelength. The similar absorption spectra were reported by various groups [7, 17, 20]. All the films show a very strong and broad UV-Visible absorption. Such a behavior is in agreement with photo-protection function of melanin and potentially useful for solar photon capture for photovoltaic applications. The exponential nature of spectra is similar to absorption spectra of typical amorphous disordered semiconductors, in which the distribution of the electronic states does not terminate abruptly at the conduction and valence band edges but tails of localized states are present in the energy gap region. To estimate the band gap of melanin films we have followed the Tauc model [21]. According to this model, the energy gap is estimated by means of an empirical optical gap (E_g) which is defined according to the following equation:

$$\alpha(E) E = B (E - E_g)^2 \quad 2$$

Where, α is absorption coefficient, B is characteristic parameter independent of photon energy, E is incident photon energy and E_g is optical band gap material. The E_g estimate can be obtained by plotting $(\alpha E)^{1/2}$ versus E and extrapolating the linear portion of the plot to the energy axis. Fig. 3(b) shows the $(\alpha hv)^{1/2}$ versus hv plots for melanin films synthesized at 3 hours. Estimated band gap of melanin films as a function of deposition time are listed in Table 1.



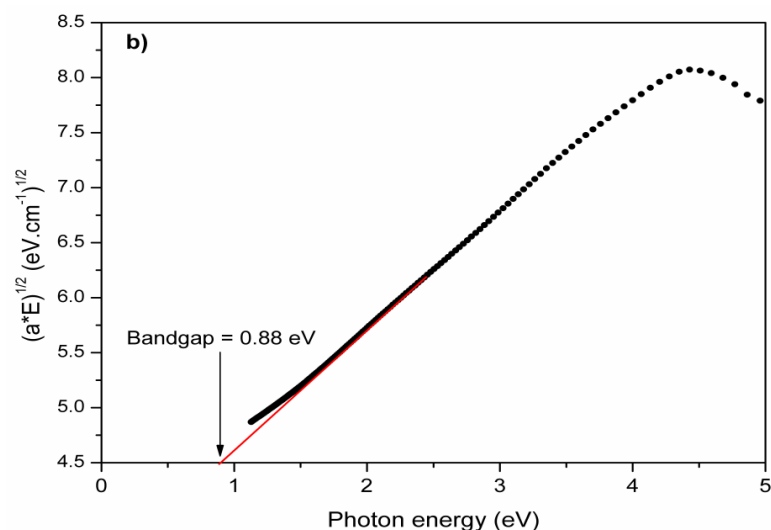


Fig 3. a) Optical absorption spectra of melanin films prepared using different deposition time b) Tauc plot for melanin film deposited using electrochemical deposition method for 3 hrs

Table 1. Relation between deposition time and optical band gap of melanin thin films

Deposition Time (Hrs.)	Estimated Band Gap (eV)
2	0.83
3	0.88
4	1.17

As seen from the table the band gap increases with increase in deposition time. It increases from 0.83 eV to 1.17 eV when deposition time increases from 2 hrs to 4 hrs. It is interesting to note that these values are smaller than the reported values of synthetic melanin [22, 23] and melanin films [24]. The narrower gap value for our melanin thin film suggests that the synthesized melanin has more disordered structure. The disorder is caused by the presence of protein fragments that were not completely removed in the isolation and purification process [14]. It may possible that some residual protein molecules may intercalated between the melanin layers which may be responsible for increase in optical gap. This inference is further strengthening from low angle XRD analysis (see fig. (1)).

3.4. Scanning Electron Microscopy (SEM) Analysis

Scanning electron microscopy (SEM) is a convenient method for studying the topography and the growth of films. Fig. (4) illustrates the SEM micrographs of the melanin films grown at 2 hrs, 3 hrs, and 4 hrs deposition time while the other deposition parameters kept constant. The scanning electron microscope (SEM) images were taken using a JEOL 6700F microscopy instrument operating at 20 kV. Before imaging, the samples were coated by sputtering with Au. As seen from the SEM images, the increase in deposition time the large aggregation of melanin macromolecules with distinct change in particle morphology. The aggregation occurs due to the increase in thickness of the films with increase in deposition time. Furthermore, the melanin films prepared by electrochemical method exhibited the dense and conformal layer without the surface defects such as voids or cracks.

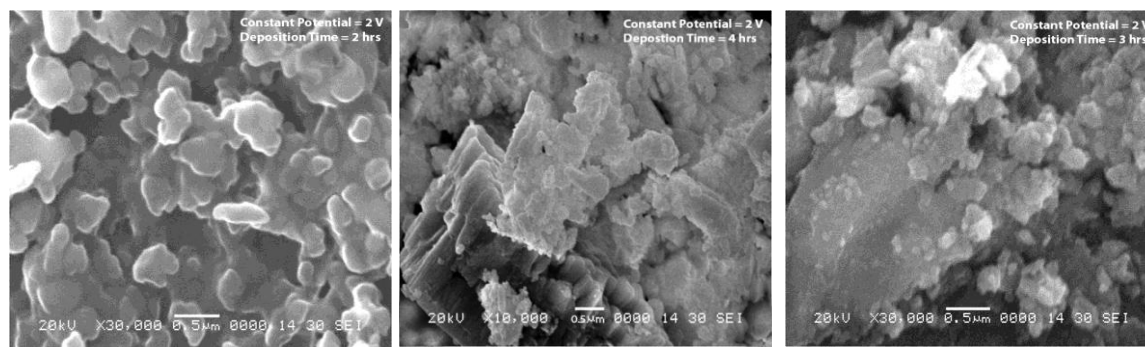


Fig 4. SEM micrographs of melanin films grown at different deposition time

By looking at the SEM images, we find that the melanin film deposited at 4 hrs of deposition time presents a rough morphological structure. However, the melanin films prepared for 2 and 3 hrs displays relatively flat and homogeneous surfaces without holes and cracks.

3.5. Raman Spectroscopy Analysis

Raman spectroscopy is considered as a versatile technique for fast and nondestructive studies of a wide-ranging number of materials. Fig. (5) shows the Raman spectra of melanin films deposited by electrochemical method at different deposition time. The Raman spectra of melanin films are similar to that of reported amorphous carbon [25] and hydrogenated nanocrystalline diamond [26/29]. For all the films the spectra exhibited two dominated peaks $\sim 1380\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$, which are related to the vibration modes of benzene like carbon sheets stacked one after another. As seen from Raman spectra with increase in deposition time the intensity of 1380 cm^{-1} peak increases and can be attributed to increase in quinine to imine in the polymerization, which is a measure of amount of polymerization [25]. The observed Raman spectra in the range $1000\text{--}1800\text{ cm}^{-1}$ may be due to superposition of various peaks. Therefore, each spectrum was de-convoluted in the entire range using the Levenberg-Marquardt algorithm [27, 28]. Typical de-convoluted Raman spectra in the range $1000\text{--}1800\text{ cm}^{-1}$ for the melanin film deposited for 4 hrs is shown in fig. (6).

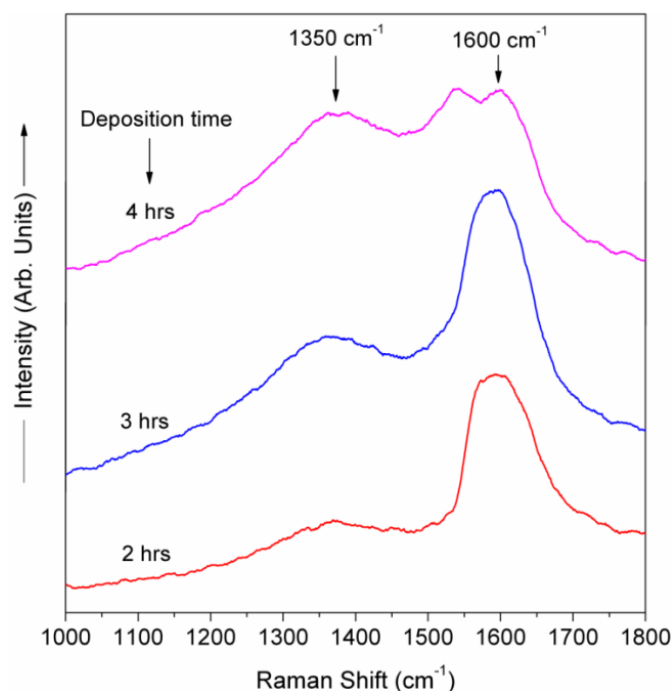


Fig 5. Raman spectra of melanin films at different deposition time

As seen from the deconvoluted Raman spectra several vibrational modes contribute to the Raman spectrum of melanin thin films. The peaks $\sim 1700\text{ cm}^{-1}$, $\sim 1605\text{ cm}^{-1}$, and $\sim 1515\text{ cm}^{-1}$ were assigned to the stretching vibration of C=O bond of ketone groups attached to the quinine, the aromatic C=C stretching modes of the basic indole structure and C=N stretching (present on the SQ structure) and/or N-H bending modes, respectively [29, 30]. The main contribution to the lower wave number region of the Raman spectrum results from a band centered $\sim 1340\text{ cm}^{-1}$ which is related to the aromatic C-N stretching mode of the indole structure. A weak contribution from the C-OH phenolic stretching and C-O stretching of the carboxylic acid those were observed $\sim 1200\text{ cm}^{-1}$. However, the Raman spectrum in the lower wave number region receive a strong contribution from a bond present $\sim 1400\text{ cm}^{-1}$ corresponding to O-H deformation vibration or combination bands due to C-O stretching and O-H deformation of carboxylic acid are reported [25, 30]. Thus, from the Raman spectroscopy analysis it is concluded that the melanin has biopolymer like structure and behave very similar to the amorphous semiconductor.

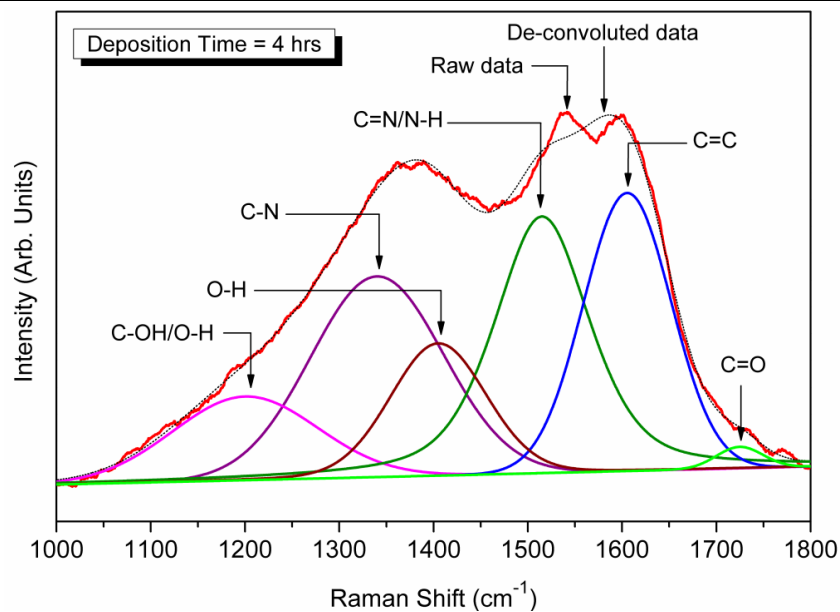
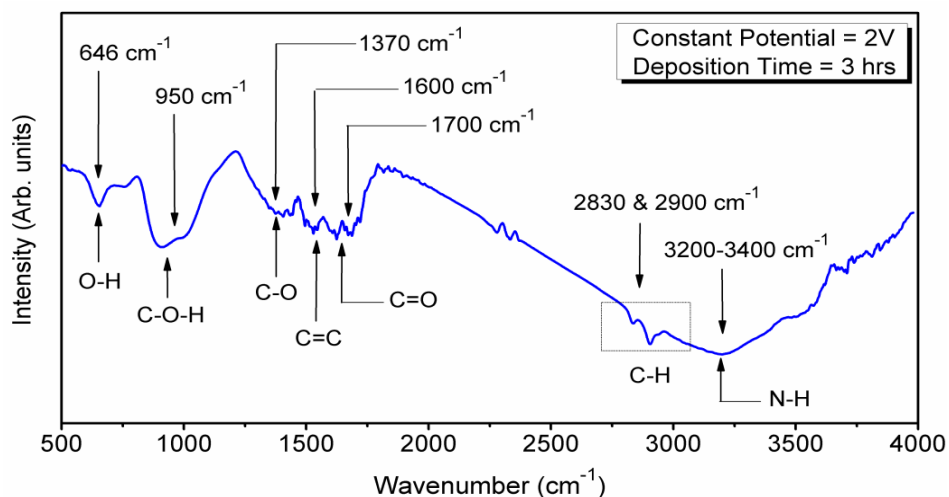
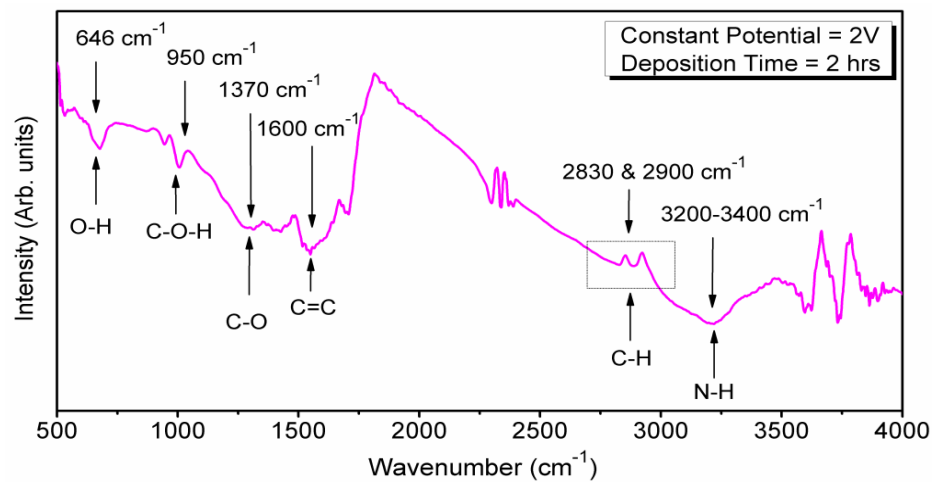


Fig 6. Typical deconvoluted Raman spectra of melanin films deposited for 4 hrs

3.6. FTIR Spectroscopy Analysis

To investigate the chemical structure of the prepared melanin thin films Fourier transform infrared (FTIR) spectroscopy was used. The FTIR absorption spectra in the range 400-4000 cm^{-1} of the melanin thin film deposited at different deposition time are shown in fig. (7). All films shows unique feature representing the characteristics of melanin.



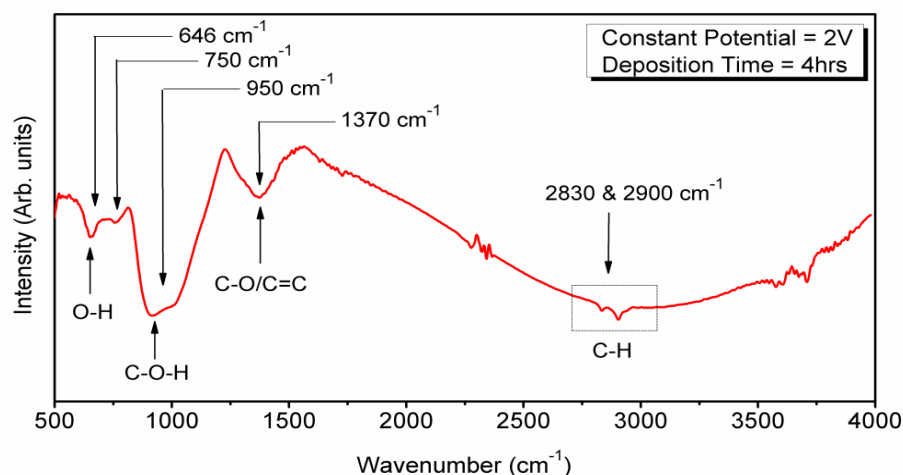


Fig 7. FTIR spectra of the melanin films prepared at various deposition time

All three spectrums show following major absorption bands of melanin thin films [31-37]:

1. A broad peak $\sim 3200\text{-}3400\text{ cm}^{-1}$ associated with the N-H stretching.
2. A peak in the range $2800\text{-}2900\text{ cm}^{-1}$ which can be assigned to stretching vibrations of C-H bonds.
3. A tiny peak $\sim 1700\text{ cm}^{-1}$ which can assigned to the C=O stretching mode of carboxylic acid (-COOH).
4. A little peak $\sim 1600\text{ cm}^{-1}$ due to the aromatic C=C bending and COO^- asymmetrical stretching
5. A broad shoulder centered near 1370 cm^{-1} corresponding to C-O stretching.
6. A broad peak centered $\sim 950\text{ cm}^{-1}$ which can associated with the C-O-H asymmetrical stretching of COOH and
7. Moderately large peak centered $\sim 646\text{ cm}^{-1}$ corresponding to O-H vibrations.

Therefore, presence of all these various absorption bands in the FTIR spectra represents the characteristic of melanin which further confirms the formation melanin thin films on ITO substrate by electrochemical deposition method.

4. CONCLUSIONS

Melanin thin films were grown directly on transparent conductive Fluorine-doped SnO_2 -coated (FTO) glass substrates using simple electrochemical synthesis method. Formation of melanin thin films has been confirmed by low angle XRD, Raman spectroscopy and FTIR spectroscopy. Structural and optical properties of synthesized melanin films were carefully and systematically studied as a function of deposition time. It has been observed that the average grain size ($d_{x\text{-ray}}$) estimated from low angle XRD analysis support the nano-aggregate model of melanin. The UV-Visible spectroscopy analysis revealed that the melanin thin films have the absorption spectra similar to that of amorphous and disordered semiconductors with strong broad band absorption in UV and Visible region. Scanning electron microscopy (SEM) images show the uniform growth of melanin films and full coverage of the substrate with controllable thickness. Fourier transform infra-red (FTIR) suggests the presence of different vibrational modes of melanin over the entire range of deposition time studied while Raman spectroscopy analysis shows the presence of vibrational modes of different functional group of melanin structure. Furthermore, investigation of the Raman and FTIR spectroscopy also shows that melanin thin films have biopolymer like structure and behave similar to the amorphous semiconductor.

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Dr. Vasant Sathe is Scientist-F at UGC-DAE-CSR, University campus, Khandawa Road, Indore 452 017. He is pioneer in Raman spectroscopy which is widely used for characterization of nano particles, films, solids, liquids and identifying different phases and to elucidate physical phenomena like, spin-phonon, electron-phonon, orbital-lattice interactions and phase transitions. He is a contributor of nearly 100 publications in international journals.



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