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1 **Formation of TiO₂ nanostructures modified Eumelanin films with**
2 **enhanced properties for biopolymer implementations**
3

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28

29 **Abstract**

30 Thin films of hybrid melanin-TiO₂ nanoparticles (eumelanin: TiO₂) deposited from solution by
31 electro-spray were accurately inspected to unveil modified structural and electronic properties
32 for device implementations. Based on the reorganization of the melanin electronic valence
33 orbital, among other interesting behaviors, we observed up to a two orders increase in the
34 absorption coefficient in the visible range. Furthermore the red-shifted absorption features,
35 disclose that the extended π - stacking of oligomers is mainly responsible for the tunability of the
36 optical gap as confirmed by photoluminescence. TiO₂ nanostructures via oxidative
37 polymerization, further improve the oligomeric character observed by means of Raman
38 scattering. Finally, the photocatalytic activity of TiO₂ nanoparticles helps the saturation of
39 shallow trap states in melanin structure and consequently enhances the charge carrier transport.

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43 Keywords: hybrid nanostructures, absorption features, spectroscopy, optoelectronics

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55 **1. Introduction**

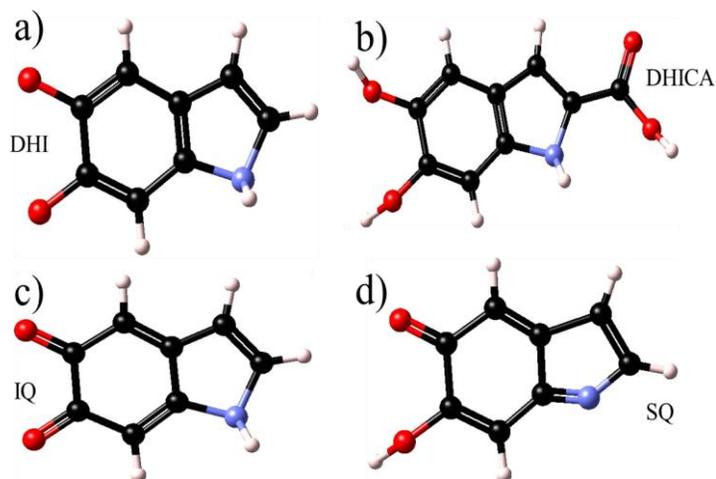
56 The recent advancements in the research of pigments like eumelanin (termed as melanin) are
57 prelude to applications of these biopolymers in the fields of bioelectronics, sensors, and
58 (opto)electronic devices [1-4]. Among the main physicochemical properties of melanin are the
59 well-known strong UV-Vis optical absorption, relatively high ionic/electronic conductivity,
60 photoconductivity (PC), exceptional biocompatibility, antioxidant and free-radical scavenging
61 activities [3,5,6]. They are at the basis of the diverse functions of the natural melanin in the
62 human body as a photoprotective agent and its involvement in some diseases like melanoma skin
63 cancer, Parkinson's and Alzheimer neurodegenerative disease. However for study purpose and
64 applications point of view, synthetic melanin guarantees a more convenient and reliable model
65 instead of natural melanin due to inherent heterogeneity and difficulty in separation of the latter
66 one [3,5]. Monomeric units of melanin structure are sketched in Fig. 1: (a) 5,6-dihydroxyindole
67 (DHI or HQ), (b) 5,6-dihydroxyindole-2-carboxylic acid (DHICA), (c) indolequinone (IQ), and
68 (d) semichinone (SQ), further details about melanin structure can be found elsewhere [3,6,7].
69 Previous studies started from characteristics of pellet type melanin samples [3], and subsequently
70 developed in various directions, allowed the study of the secondary structure and the dependence
71 of functional properties on the molecular organization and film quality [4,7,8]. Comprehensive
72 results were obtained in terms of film smoothness, continuity and overall quality, followed by
73 controlled structural, electronic and optoelectronic properties that have connected the
74 fundamental features of the melanin organization, its feasible functionalizations [5,6,9] and
75 practical applications [3,10-13].

76 An intriguing aspect of this research is involving the interactions of melanin with other organic
77 or inorganic nanoparticles in hybrid/nanocomposite materials. Most common drawbacks are
78 complete insolubility in organic solvents, the lack of appropriate deposition techniques that
79 prevent the development of homogeneous and reproducible blended thin films, and the lack of a
80 solid conceptual frame to understand the structure–property–function relationships upon the
81 interaction of nanoparticles with synthetic melanin, hindering the full implementation of the
82 bio(electronic) devices.

83 Titanium dioxide (TiO₂) nanoparticles are low cost, non-toxic, stable oxide semiconductor with
84 distinctive physical and chemical properties, applied in some photovoltaic devices and several

85 photocatalysts applications. The combination of metal/metal oxide nanoparticles like TiO₂ with
86 organic structured materials is very attractive for the electronic, morphological properties
87 modifications [14-17] and towards practical applications. To date, the formation of hybrid
88 functional materials based on TiO₂ and monomer precursors, like DHICA were established using
89 different synthesis methods i.e., DHICA polymerization through coated TiO₂ nanoparticles and
90 solution mixed DHICA/TiO₂ hybrid nanostructures [18,19], but complete picture of such hybrid
91 materials in the form of thin films, ideal to investigate nanohybrid materials is still lacking.
92 Hence, melanin-TiO₂ nanostructure is an open issue for understanding the mechanism of hybrid
93 formation, as their properties are strongly dependent on the particle size and aggregation
94 mechanisms that vary while passing from solution to the solid film.

95 Here, we report the fabrication of melanin blended TiO₂ nanoparticle thin films by solution
96 processed electrospray deposition (ESD) technique. The aim to develop thin films of these kind
97 of hybrid nanostructures was multifold: the foremost, is to enhance the photo absorption for
98 extended range of wavelength by exploiting the broadband absorption of melanin and TiO₂
99 nanoparticles. Also important is the response of melanin coupled to strong electron
100 acceptor/donor materials. Last but not least, the structure-function relation and mutual
101 dependence of these components must be critically investigated. By the way, properties of
102 melanin (particularly the transport) are complicated by the presence of two kinds of water, the
103 weakly and strongly bounded to the structure [3,6,9]. Adding the TiO₂ which has been widely
104 used for water splitting, purification or treatment applications will bring experimental
105 insights for the charge transport mechanisms and its response towards charge carrier
106 recombination activities. In addition, the motivation of this work was to explore in details the
107 characteristics of melanin and melanin: TiO₂ nanoparticle active layers, when heated at a high
108 temperature as required for many device preparations (T> 120°C). To investigate all these issues,
109 we analyzed morphological, structural, electrical and optical properties of the active layer
110 melanin and blend (melanin: TiO₂) thin films for as prepared and treated samples, grown by ESD
111 deposition technique looking forward to organic/inorganic photovoltaics and other
112 (bio)electronic device applications.



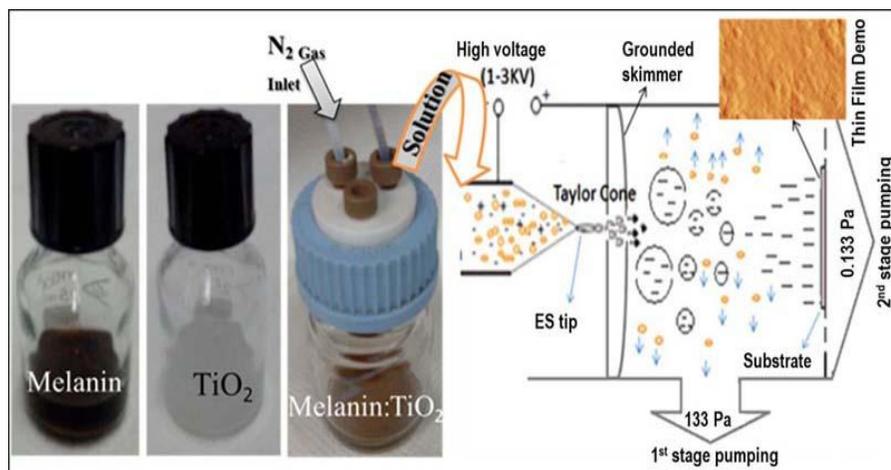
113
 114 **Fig. 1.** Monomeric units for melanin structure: (a) DHI or HQ, (b) DHICA, (c) IQ, (d) SQ. Red
 115 (oxygen atoms), light blue (nitrogen atoms), white (hydrogen atoms), and black (carbon atoms).

116 2. Experimental details

117 Synthetic melanin powder, prepared by oxidation of tyrosine with hydrogen peroxide (M8631
 118 synthetic melanin) and TiO₂ nanoparticles (about 25 nm) were purchased from Sigma-Aldrich.
 119 Melanin is notoriously insoluble pigment, but dimethyl sulfoxide (DMSO) is the most effective
 120 solvent for its use. We dissolved melanin in Dimethyl Sulfoxide Methanol Solution (DMSO:
 121 CH₃OH; 1:20) with the concentration of 0.2 mg/ml. Similarly, for TiO₂ solution we used the
 122 same concentration of 0.2 mg/ml but different solvent (dichlorobenzene). After the preparation
 123 of the solution, the melanin and melanin: TiO₂ (with 1:1 ratio) were deposited by electrospray
 124 technique on indium-tin-oxide (ITO) and corning glass substrates. To realize the formation of
 125 hybrid nanostructures through enhanced interfaces area the melanin and TiO₂ proportion were
 126 kept the same, without going into the details of ratio optimization, which is essential for the
 127 purpose of efficient electronic devices in the future and is beyond the scope of this paper.

128 The schematic of ESD developed system [20,21] during thin films deposition is presented in the
 129 Fig. 2. A solution container was pressurized with the N₂ gas and the flow rate was controlled by
 130 measuring the time required to move a solution of 20 μL through 1 cm gap marked at various
 131 position on Teflon tube. The flow rate (1.3 μL/s) and applied voltage (2 kV) were kept constant
 132 during the deposition [6]. ESD melanin and blend films of the average thickness of 200 nm on

133 glass and ITO substrates were characterized with various microscopic and spectroscopic
134 techniques.



135
136 **Fig. 2.** Schematic of the ESD system used for the film growth on respective substrates.

137
138 The morphological studies of these melanin and blend films were performed by Scanning
139 Electron Microscopy (SEM- SU-1500 Hitachi) operating at 2–5 kV and Atomic Force
140 Microscopy (AFM- Agilent’s Pico Plus) working in tapping mode with cantilever frequency 160
141 kHz. The AFM images were analyzed quantitatively by Gwyddion Software [22]. Optical
142 absorption spectra of melanin and blend films were measured in the ultraviolet, visible and near
143 infrared regions. Absorption measurements were carried out by measuring the absorption light
144 intensity obtained by spectrophotometer (Perkin, Elmer Lambda 950 UV/Vis/NIR).
145 Photoluminescence (PL) study was carried out by using Dongwoo Optron W500i with He-Cd
146 laser having wavelength 325 nm (3.8 eV) for excitation purpose.

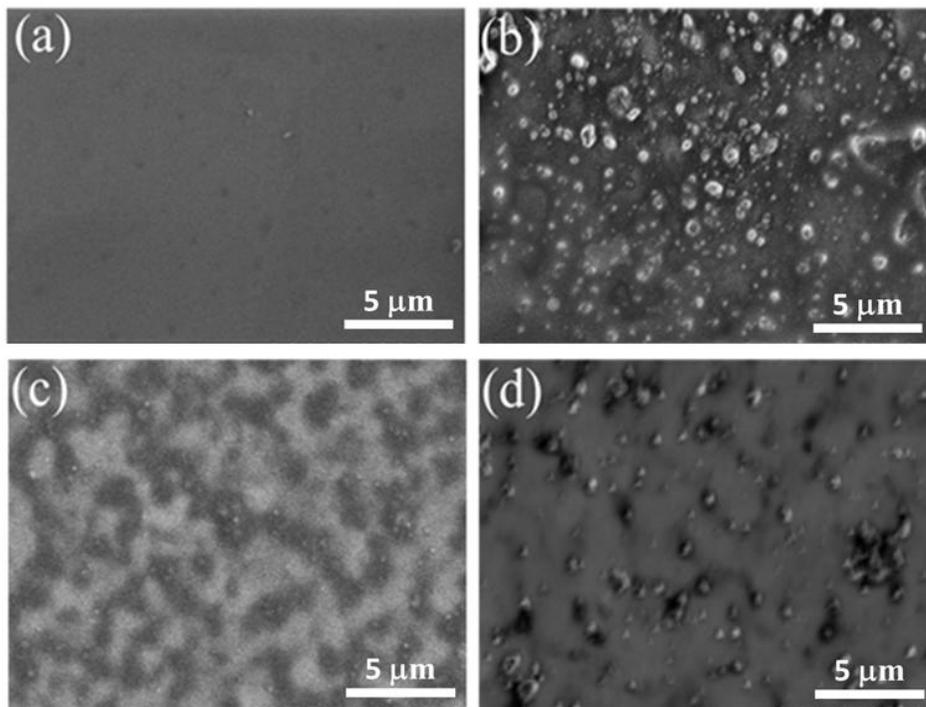
147 The identification and investigation of functional group vibrations of melanin and blend
148 (melanin: TiO₂) were performed using NICOLET 6700 Fourier Transform infrared spectroscopy
149 (FTIR). Argon ion laser with laser lines, of wavelength 514 nm as excitation source was used in
150 dark ambient at room temperature for Raman spectra (Renishaw 1000). Finally, the electrical
151 characterization was taken under the dark and illumination conditions. The current–voltage (J –
152 V) curves were obtained by using a Keithley 4200 semiconductor analyzer in dark and under
153 illumination of an AM1.5 (100 mW/cm²) calibrated with IL1400BL radiometer. Gold stripes
154 were evaporated with a channel length of 50µm onto glass substrates after film deposition to get

155 planar geometry for J – V measurements in both forward and backward voltage sweep directions.
156

157 **3. Results and discussion**

158 **3.1. Film morphology**

159 The morphology of synthetic melanin film is quite different and of better quality than that of
160 natural melanin, due to the successive improvements in the methods of fabrication and the choice
161 of solvents that affect the structure, and thin film quality [8,23,24]. In the present work, we
162 report the thermal heat treatment effect on the morphology of synthetic melanin film and of its
163 blend with TiO₂ nanoparticles. Previously [6], we found that the pure melanin thin films
164 deposited at 3 kV applied voltage by ESD technique showed 2D regions with separated
165 boundaries between flat zones formed on sample surface due to strain and to the process of
166 drying. Therefore, here in this work we effectively lowered the applied voltage to 2 kV, for all
167 the samples. SEM analysis show that the thin films fabricated at 2 kV by controlled electrospray
168 deposition process [6,20] are quite homogenous, with complete flat coverage of the substrate
169 with planar regular structures without any cracks or boundaries as shown in Fig. 3(a-d). SEM
170 images for the annealed (at 120° C for 5 minutes) samples deposited on glass were presented in
171 Fig. 3(a and b) for melanin and melanin: TiO₂ blended films respectively, while same annealed
172 samples deposited on ITO substrate are in Fig. 3(c and d). Annealing is particularly important in
173 the case of the hybrid films, to reach an acceptable homogeneity. The pristine hybrid film on ITO
174 substrate (not shown here) indicated small clusters of TiO₂ nanoparticles coated and /or wrapped
175 by melanin polymorphic organized layers. After annealing, the homogeneity of the blend film
176 enhanced significantly and moderate distribution of TiO₂ nanoparticles (Fig. 3(b and d)) on the
177 whole substrate was observed. Thermal annealing certainly affects the uniformity of thin films
178 deposited on all kinds of substrates especially the conducting surfaces. In discussing samples
179 deposited on glass substrates (upper panel) vs. samples on ITO substrates (lower panel) in Fig.3,
180 the latter ones probably exhibited more wetting character in the blend film, preferentially due to
181 the interaction between melanin and titania nanoparticles or interfaces with the substrate. These
182 observations are favorable to conditions of molecular orbital hybridization and functionalization
183 to be employed in real devices.

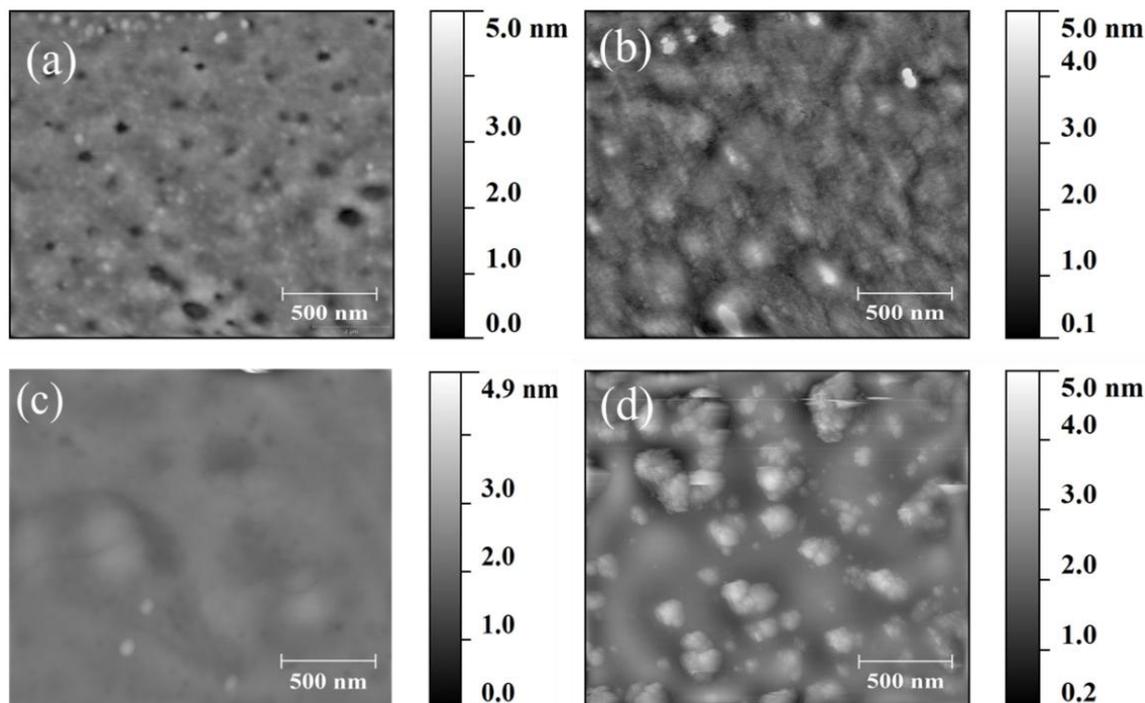


184

185 **Fig. 3.** SEM images comparison: (a) melanin film on glass substrate; (b) blend (melanin: TiO₂) on glass
186 substrate; (c) melanin film on ITO substrate; (d) blend (melanin: TiO₂) on ITO substrate. Furthermore, all
187 SEM images were from samples annealed at 120° C.

188 AFM images of melanin and blend (melanin: TiO₂) deposited on glass (upper panel) and ITO
189 substrate (lower panel), after heat treatment are reported in Fig. 4, respectively. While comparing
190 annealed melanin thin films grown on ITO with those on glass substrates, the first one shows
191 clear improvement in the surface morphology, in terms of film roughness, homogeneity and
192 oligomers structures planarity, as shown in Fig. 4(a and c). AFM images of blended titania films
193 annealed at 120°C are reported in Fig. 4(b and d). Thermal annealing might affect polymers film
194 thickness, by a more organized molecular spacing and in addition, helping supramolecular
195 aggregation with increased uniformity and film quality. It is evidenced from the images that the
196 signatures of titania nanoparticles are very clear, especially on ITO substrates, and showed
197 almost no difference in root-mean-square roughness (before annealing 1.02 nm – after annealing
198 1.05 nm) associated with different regions of the blend film after annealing. In case of melanin
199 films in the left panels of Fig. 4, the morphology disclosed overall uniform lengthened platelet
200 [6,8]. Compared to the latter, slightly corrugated surface of melanin: TiO₂ samples (right panel
201 of Fig. 4) was observed when blended with polymers by solution process, obviously due to

202 presence of titania particles agglomeration (although reduced with annealing) [15]. As a final
203 observation, the films grown on conducting surfaces (Fig. 4d) with better adhesion are highly
204 organized in terms of substructures, supported by the optical analysis in the coming section.



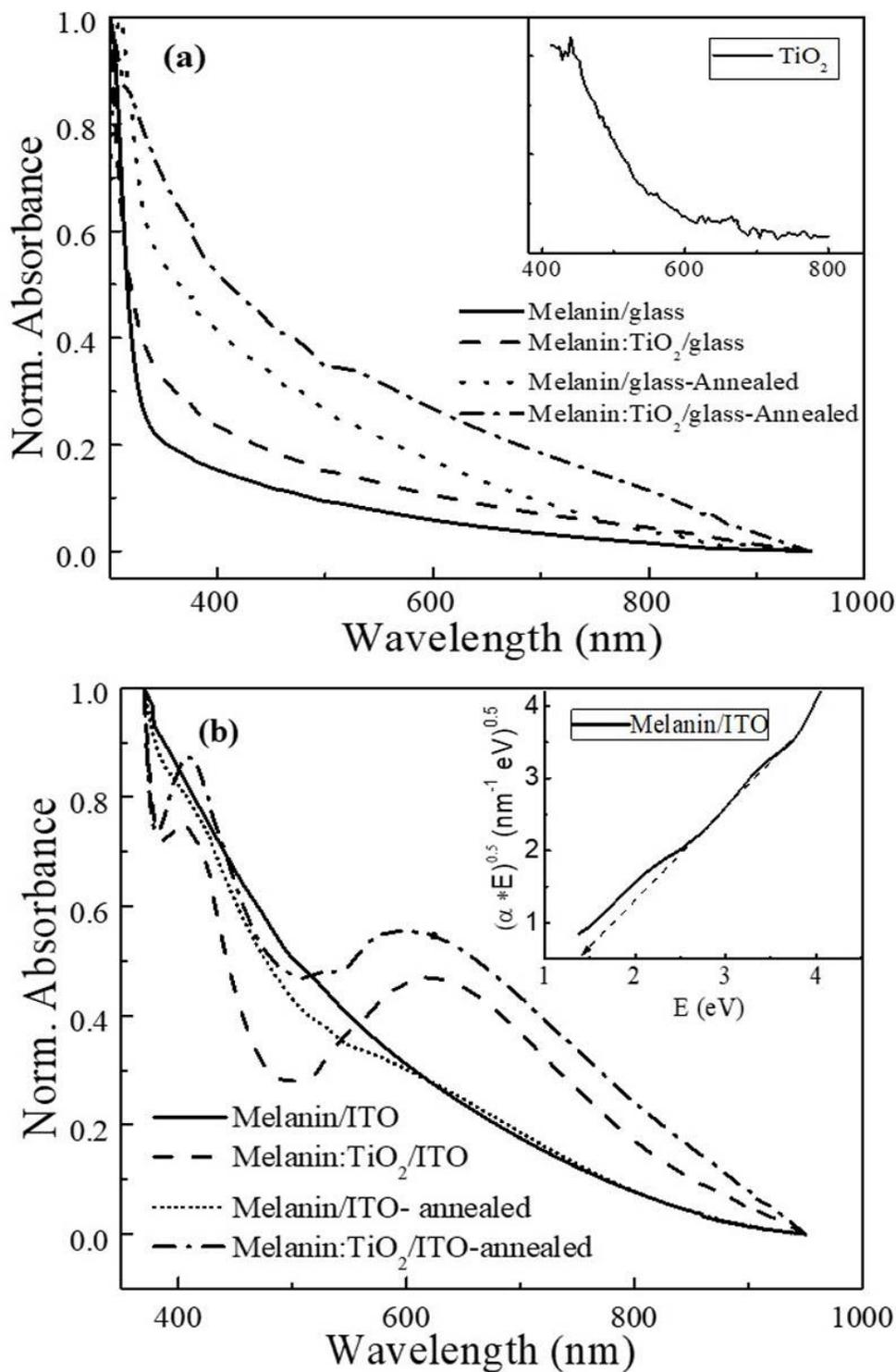
205
206 **Fig. 4.** AFM images in tapping mode of melanin thin film deposited on glass substrate (a), and melanin:
207 TiO₂ blend on glass substrate (b) - (upper panel). AFM image of melanin thin film deposited on ITO
208 substrate (c), and blend (melanin: TiO₂) deposited on ITO substrate (d) - (lower panel). Here, we
209 presented the samples annealed at 120° C.

210 3.2. Optical absorption

211 The normalized absorption spectra of thin films melanin and its blend with TiO₂ as prepared on
212 glass and ITO substrates were determined in the region (300- 950 nm) and shown in the Fig. 5(a
213 and b), respectively. Before annealing the absorption spectra of melanin, particularly on glass
214 substrates (Fig. 5(a), solid curve), showed the typical wide band character consisting of overall
215 featureless smooth absorption without any apparent edge. However, an increase in absorption
216 spectra in the visible wavelength range (380-750 nm) observed for pure melanin films, after
217 annealing (Fig. 5(a and b), solid and dot curves) is suggesting more compact films (especially
218 on conducting substrate, probably due to adhesion properties of melanin [25,26]), and improved

219 self-assembly relating to monomeric components bonding. The most intriguing results were
220 obtained after embedding TiO₂ nanoparticles in the melanin matrix particularly on conducting
221 surfaces. The blended (melanin: TiO₂) dash and dash dot curves in Fig. 5(a and b) show
222 enhanced absorption spectra compared to melanin, due to the photocatalytic activity of TiO₂
223 nanoparticles and better mutual adhesion during the ESD process [21,27]. Moreover, the
224 normalized absorption spectra of melanin blending TiO₂ nanoparticles on ITO substrates showed
225 (Fig. 5b) completely twisted behavior composed of new features different from the melanin
226 characteristic broadband monotonic absorption [3,5]. These spectra with even broader and
227 dominant absorption (350-800 nm) are similar to the prominent absorption of conventional low
228 band gap conducting polymers in the range of 400-750 nm due to π - π bonding [15,20]. The peak
229 observed near UV region at about 350 – 400 nm is due to the fundamental absorption of the Ti-O
230 bond at that wavelength as shown in the inset of Fig. 5(a). Moreover, the wet nature of ESD thin
231 films on ITO substrates reflect the slow growth rate for the dynamics of molecular
232 organization/oligomerization, as compared to the fast growth rate on non-wet insulating glass
233 substrates. These effects on conducting substrates were also accompanied by slight differences in
234 morphology observed in SEM and AFM analysis. In addition, the photocatalytic properties of
235 TiO₂ nanoparticles also played a significant role in the DHICA/DHI polymerization [19] that
236 alters the absorption spectra of melanin in a different fashion from that of amorphous
237 semiconductor [3]. Although melanin layer absorption features on conducting surface in the UV-
238 Vis-NIR range are in agreement with the previous experimental observations [4] and theoretical
239 simulations [28,29], and attributed to an increase in the degree of π -stacking and to the oxidation
240 state of melanin, we emphasize here that the presently observed physical properties are the
241 consequence of a controlled film fabrication by efficient ESD system able to blend melanin with
242 TiO₂ nanoparticles which leads to a photocatalytic oxidative action on conducting surface. These
243 examined absorption features are enhanced under thermal annealing with an increase of two
244 orders of magnitude of absorption coefficient around 600 nm (Fig. 5b) in comparison to pure
245 melanin suggesting the augmented adhesion between the two constituents. In fact, melanin
246 similar to polydopamine [17,25] shows significantly strong adhesion to TiO₂ nanoparticles in the
247 hybrid structure due to catechol groups.

248 We recently applied the Tauc model [4,24,30,31] for the calculation of energy gap value from
249 the optical band edge as the absorption curve is not showing any of the exponential behavior of



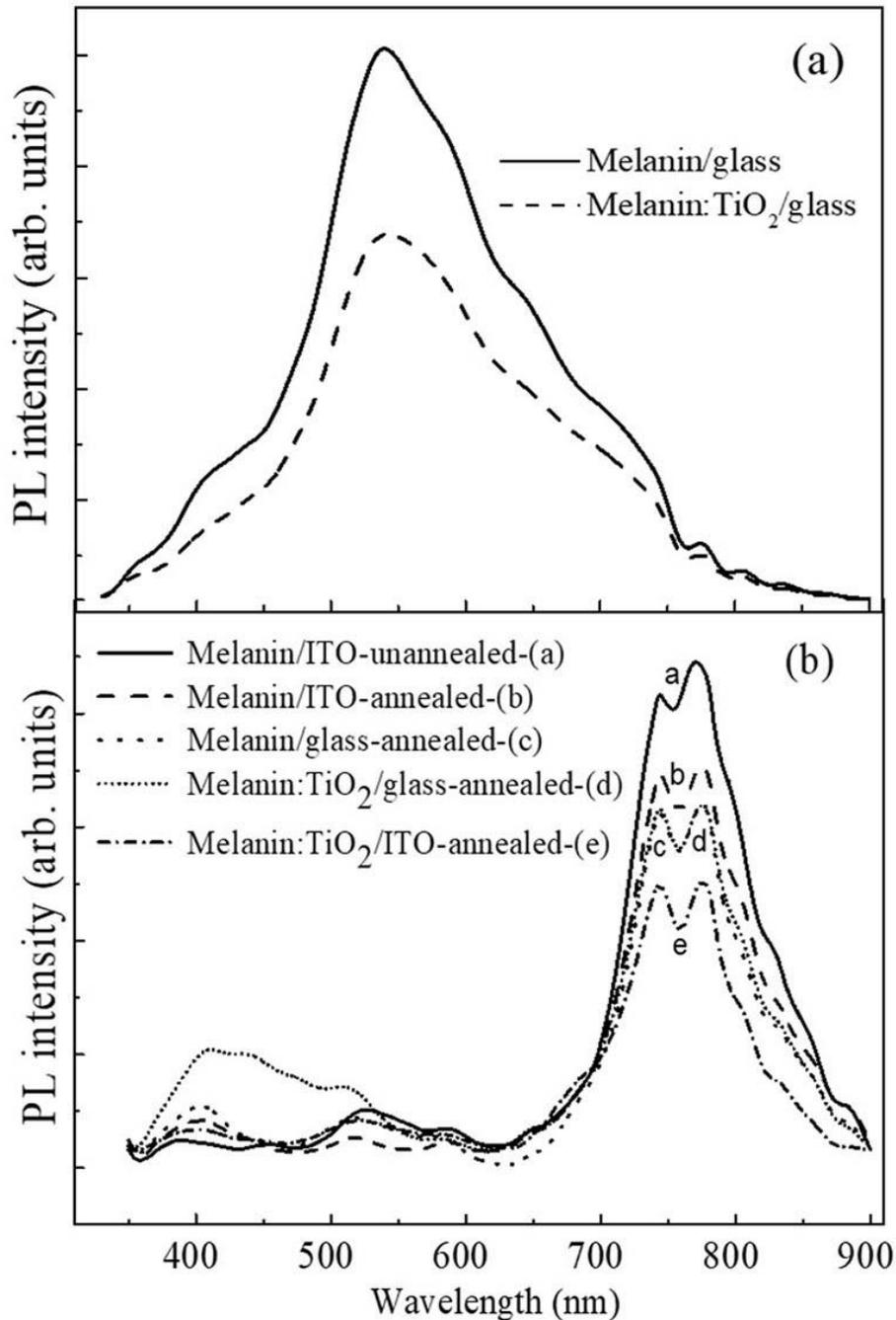
250

251 **Fig. 5.** Normalized absorption spectra of melatonin and its blend (melatonin: TiO₂) films on glass and on ITO
 252 substrates are shown in Fig. (a) and (b), respectively. The absorption spectra of TiO₂ nanoparticles
 253 deposited on ITO substrate by ESD deposition is reported in the inset of (a) and energy band edges of
 254 melatonin film on ITO is described in the inset of (b), respectively.

255 more disordered natural melanin. Equation of the form $(\alpha h\nu)^{1/2} \propto (h\nu - E_g)$ according to the Tauc
256 model for indirect band gap semiconductor was used, where α is the absorption coefficient
257 (obtained from the absorption curves in Fig. 5), $h\nu$ is the incident photon energy on the sample,
258 and E_g gives the optical gap value by plotting the term $(\alpha h\nu)^{1/2}$ as a function of energy. The result
259 of extrapolated onset on the horizontal axis of the absorption curves for a set of all films in this
260 study was in the range of 1.25- 1.55 eV. The optical gap value 1.4 eV for melanin film deposited
261 on ITO substrates was obtained using the Tauc plot as shown in the inset of Fig. 5(b). The
262 estimated energy band gap values for melanin are slightly dependent on the choice of substrates,
263 annealing and on the interaction of TiO₂ nanoparticles as photocatalytic that induced stacking
264 ordering in the polymeric chains. These values are comparable to the melanin E_g values observed
265 in the range from 1.0 to 1.4 eV [4,6,24,30,32,33,34]. We must be aware of the effect of Mie
266 scattering that may be present at the longer wavelengths in the tail part of the spectra [3,4,6,9]
267 affecting the energy band edge.

268 **3.3. Photoluminescence spectroscopy**

269 To examine further the optical properties of melanin and blend films of melanin: TiO₂ a PL study
270 was carried out at room temperature in order to understand the interaction between the two
271 components. As a comparison, Fig. 6(a and b) show the PL spectra of melanin and blend thin
272 films excited with the excitation wavelength of 325 nm. It is found that different behavior of the
273 PL spectra in the range of 300– 950 nm before annealing supports the significant substrate
274 effects obtained previously from morphological and absorption analysis. The emission spectrum
275 for 325 nm (3.8 eV) excitation reached the peaks maximum at around 550 nm obtained from
276 melanin on glass substrates and then decreased monotonically with increasing emission
277 wavelength [32,35], while the emission spectrum for melanin: TiO₂ blend on glass substrates
278 (Fig. 6a) was reduced due to incorporation of the TiO₂ nanoparticles in the melanin matrix.
279 Similar emission spectra related to the DHICA anions were obtained with maximum peak
280 intensity at wavelength of 425 nm [19] compared to 550 nm in this case. Furthermore, it has
281 been shown in the literature that melanin PL quantum yield is small, proved by the probe beam
282 attenuation method and origin of some unexpected observations [7,26,36]. We supposed that the
283 reason of unforeseen wide PL (FWHM ~ 1eV) behavior of pure melanin and blend films, on
284 insulating substrates could be that the exciton emission originating from a hole-electron



285
 286 **Fig. 6.** (a) PL spectra of melanin and blend samples deposited on glass substrates before annealing. (b) PL
 287 spectra of melanin and hybrid melanin: TiO₂ samples deposited on insulating and conducting substrates
 288 before and after annealing at 120° C for 5 minutes. All PL spectra were recorded with He-Cd laser having
 289 excitation wavelength 325 nm (3.8 eV).

290 recombination, was most probably due to trapped states on the surface [15], resulting from the
291 combination of disorder of melanin monomers, defects (oxygen vacancies/structural defects due
292 to agglomeration) and impurities including two kinds of water bonded in structure of melanin.
293 Such impurities and defects could be eliminated by thermal, physical or chemical processes. In
294 the case of thin films of organic species such as melanin and its blend with TiO₂ anatase phase
295 over the ITO conductive (Fig. 6b) layer, electron and hole scavengers and the charge
296 recombination mechanism in the visible and up to near infrared region are dominant [26,37,38].
297 The PL spectra after annealing (Fig. 6b) for a set of samples were shifted to an energy gap values
298 near IR region (700- 900 nm) compared to that on glass substrates before annealing in the
299 wavelength range 350-550 nm. Such observations are suggesting that the recombination of a hole
300 with an electron due to surface trapped states/ disordering was reduced after annealing. The
301 intense peaks in overall spectra for melanin and titanium dioxide were observed at the high
302 wavelength near IR band gap region (Fig. 6b) for melanin, suggesting larger π -stacking
303 oligomerization related to red-shifts in the absorption spectra and then emission. The intense
304 excitation peaks in annealed PL emission spectra of the thin films started at offset of 1.3-1.45 eV
305 and reach their maximum at 1.55 eV. These observations are in agreement with the estimated
306 band gap values obtained from absorption analysis. The PL peaks (probably affected by
307 spectrometer background) in the range of 1.5- 1.65 eV may correspond to different
308 chromophores [3,7] of melanin DHI and DHICA, the latter one at lower energy compared to
309 DHI that has dissimilar reaction times and extinction coefficients at different wavelengths [39].
310 In the Fig. 6(b), these observations further elucidate the trend of PL peaks intensity that
311 quenched significantly in a systematic way from the pristine melanin/ITO film (curve-a) by
312 annealing the same sample (curve-b) and then by adding TiO₂ nanoparticles as an electron
313 acceptor with respect to the donor melanin material (curve-e). It reveals the strong interface
314 formation between melanin and TiO₂ nanoparticles as a nanohybrid structures fostering robust
315 devices applications. On the contrary, on insulating surface almost the same PL peaks intensity
316 for thin films of melanin/glass (curve-c) and the blend/glass (curve-d) are observed, suggesting
317 the weak interface formation between melanin and TiO₂ nanoparticles, that results in the TiO₂
318 nanoparticles PL response at around the wavelength values (450-550 nm).

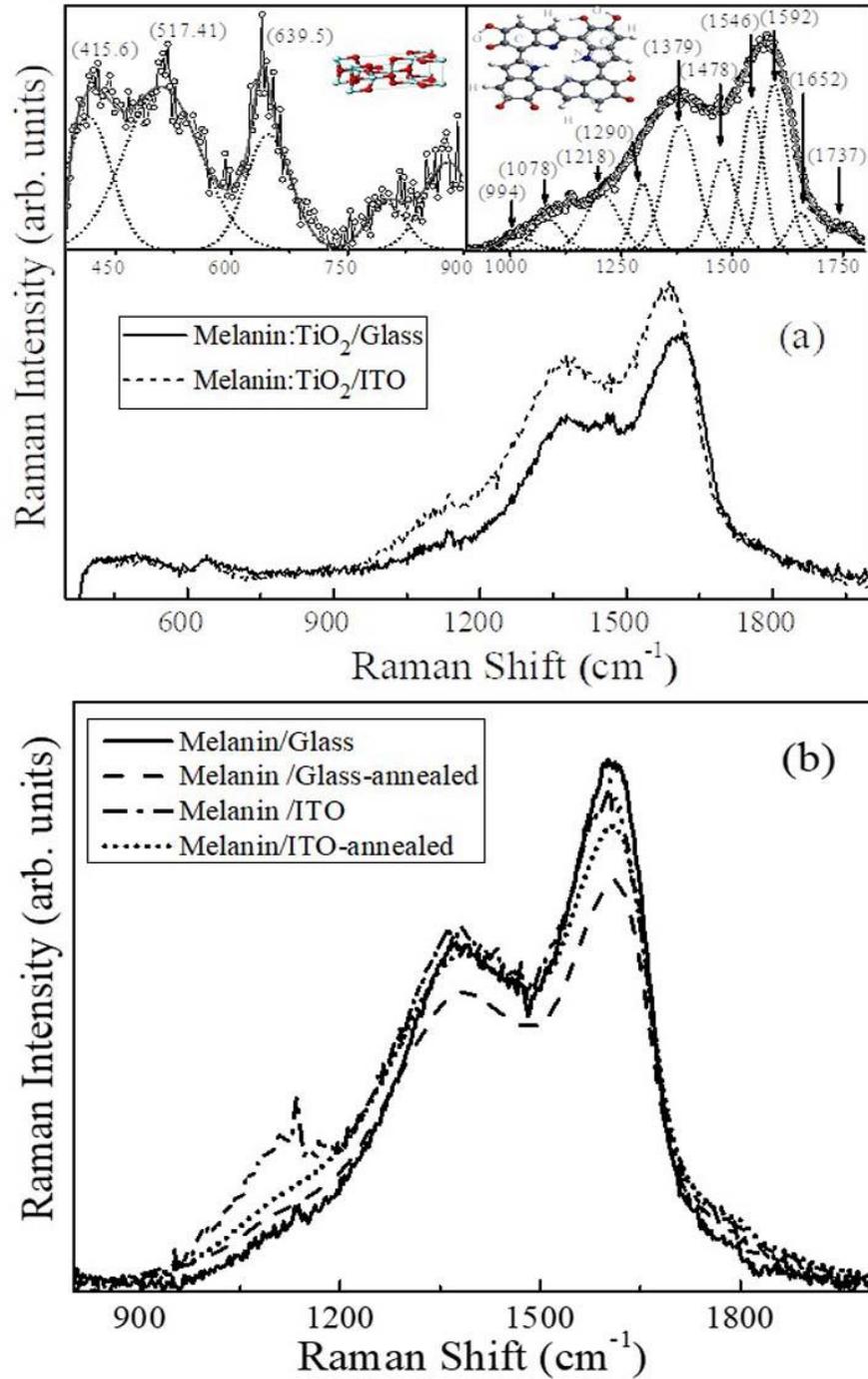
319 To put into relation the absorption and PL spectra, we observed an increase in the absorbance
320 with dominants absorption feature for melanin: TiO₂ samples and unusual emission spectra from

321 PL spectroscopy. The comparison of annealed melanin: TiO₂/ITO absorbance (in Fig. 5(b),
322 dash-dot curve) and PL spectrum shown in Fig. 6 (curve-e) revealed our observations further.
323 Here, we must point out that efforts are required to quench completely the PL spectra for the
324 melanin-TiO₂ hybrid nanostructures peculiarly presented here in the near IR band gap region.
325 For such a complex nanohybrid system, this could be done in the future by balancing the charge
326 carrier mobilities while changing the ratio of melanin: TiO₂ (1:1) nanoparticles that will
327 eventually reduce charge recombination processes.

328 3.4. Raman and Fourier transform infrared spectroscopy

329 Raman spectra were collected from melanin and its blend with TiO₂ (Melanin: TiO₂) films which
330 were deposited on glass and ITO substrates through ESD technique. All ESD films investigated
331 through visual inspection with microscope and by Raman spectroscopic analysis were quite
332 homogenous, which permitted their study by a spatial resolution on the surface of the samples
333 around 1 μm [6]. The Raman spectra of melanin are similar to the amorphous carbon graphitic
334 structure having two dominant peaks at about 1600 cm⁻¹ and 1300 cm⁻¹, which are related to the
335 vibrational modes. These vibrational modes involving different atoms (carbon, oxygen, nitrogen
336 and hydrogen) are organized according to different functional groups, bonded to indolic structure
337 that gives the formation of basic monomeric units of melanin such as DHI, DHICA, SQ and IQ.
338 The Raman spectra of thin films taken at room temperature consists of Raman active vibrational
339 modes involving these different functional groups like, hydroxyl groups OH, carbonyl groups
340 C=O, carboxylic acid COOH and NH groups, as reported in Fig. 7. In blended samples a slight
341 shift was observed in main G (~ 1600 cm⁻¹) and D band (~ 1300 cm⁻¹) of carbon structures due to
342 incorporation of TiO₂ nanoparticles of anatase phase. Moreover, the G and D band on ITO
343 substrates were more intense than on glass. The Raman spectrum was fitted using the Gaussian
344 function indicating the melanin (900-1800 cm⁻¹) and anatase TiO₂ (400-900 cm⁻¹) vibrational
345 modes. The enclosed fitted area of blended Raman spectrum is reported in the left inset of Fig.
346 7(a) that indicates the presence of TiO₂ nanoparticles modes in the range of 400-900 cm⁻¹. The
347 spectrum exhibit Raman fingerprints for anatase phase with important modes B_{1g} (419 cm⁻¹), A_{1g}
348 (517 cm⁻¹) and E_g (639 cm⁻¹) in agreement with previous results [40].

349 In the recent literature, nine and eleven components fitted Raman spectrum has been already
350 observed which were correlated with different vibrational modes of melanin [6,41]. In Fig. 7(a),



351

352 **Fig. 7.** (a) The normalized Raman spectra of blend (melanin: TiO₂) deposited on ITO and glass substrates,
 353 the inset showed the fitting plot of the experimental Raman spectrum along with chemical structure for
 354 both melanin (right) and TiO₂ (left), respectively. (b) Raman Spectra for melanin on ITO and glass
 355 substrates, before and after annealing of 120 °C.

356

357 **Table 1.** Raman Peaks related with modes in melanin blended TiO₂ nanoparticles complex system.

358	Raman Peaks (cm-1)	Assignments
359	Melanin Peaks in blend (melanin: TiO ₂)	
360	994 ± 2	O-H out of plane deformation
361	1078 ± 2	C-H deformation modes in or Out of plane
362	1218 ± 2	N-H in plane deformation and stretching C-C ring breathing
363	1290 ± 2	C-O stretching and OH deformation in COOH
364	1379 ± 2	Stretching (C-N)/indole ring vibration
365	1478 ± 2	C=C and C=N in plane vibration in pyrrole
366	1546 ± 2	Pyrrole ring stretching vibration/ C=C aromatic
367	1592 ± 2	Indole ring vibration / stretching antisymmetric (COO-)
368	652 ± 2	C=C aromatic ring vibration
369	1737 ± 2	Stretching C=O in DHICA, Quinone or Ketone
370	TiO ₂ Peaks in Blend	
371	639 ± 2	E _g mode for anatase TiO ₂
372	517 ± 2	A _{1g} mode for TiO ₂
373	415 ± 2	B _{1g} mode for TiO ₂

374

375 the Raman spectra of blended films confirmed that titania nanoparticles are not perturbing the

376 spectral response of melanin functional group. The best-fitting curve of melanin experimental

377 Raman spectrum composed of ten components is shown in the right inset (zoomed from solid

378 curve) of Fig. 7(a). The peaks around 800 to 1000 cm⁻¹ in the melanin structure are due to the

379 deformation of modes of vibration in the pyrrole and indole structure. The broad peaks about

380 1400 cm⁻¹ overlap different vibrational modes namely C=C, C=N ring stretching in pyrrole

381 structure. The lower intensity bands around 900 – 1200 cm⁻¹ are due to the vibration modes of

382 CH, OH and NH with in plane or out of plane deformation. The broad band feature at 1550 and

383 1622 cm⁻¹ is the contribution to the Raman bands of pyrrole and indole ring stretching vibrations.

384 The peaks centered at about 1700 and 1775 cm⁻¹ related to the C=O stretching vibrational modes

385 in carboxylic acid or in quinone or ketone group. However, at 1775 cm⁻¹ and above weak peaks

386 are observed corresponding to the stretching of carbonyl functional group vibrations in

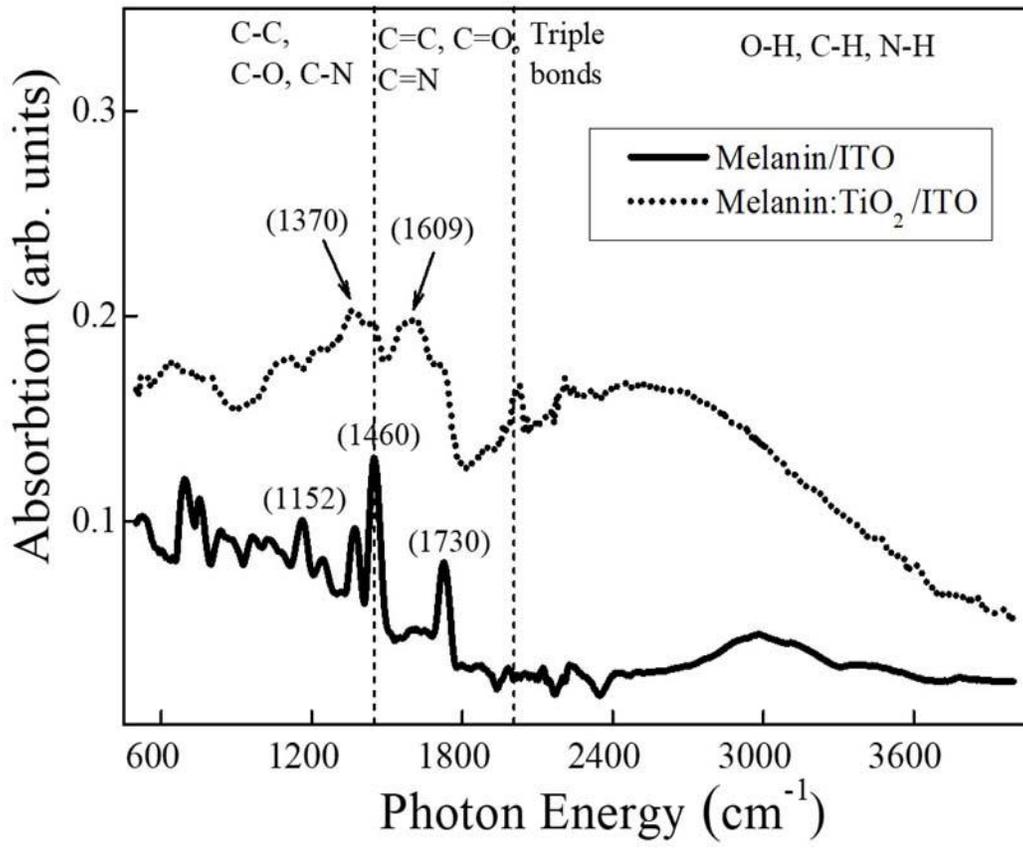
387 carboxylic acid [42]. The pyrrole di- and tri-carboxylic groups are also investigated during the

388 subsequent oxidization of DHI and DHICA, which described the structure of melanin [43].

389 These Gaussian peaks value corresponding to the various vibrational modes for melanin and
390 TiO₂ anatase peaks in the melanin: TiO₂ sample obtained from the fitting of the experimental
391 Raman spectrum are listed in Table 1.

392 On the other hand, Raman spectra of the melanin on glass and ITO substrates before and after
393 annealing are given in Fig. 7(b). It is important to note that the Raman spectrum of the melanin
394 on glass reflect the structure like graphitic amorphous carbon, with a band D at 1300 cm⁻¹ and a
395 strong band G at 1600 cm⁻¹ [6,41]. A small shift was observed in the G band position of melanin
396 spectra deposited on ITO compared to glass substrates, and after annealing compared to as
397 prepared melanin film on ITO. This regular small shift in the position of G strong band after
398 annealing of melanin Raman spectra is similar to aromatic character changing from amorphous
399 carbon graphitic structure to nanocrystalline diamond and/or nanocrystalline carbon graphitic
400 structure. Furthermore, the shift in the G position is related to the optical Tauc gap [44],
401 supporting our results obtained from absorption and PL analysis.

402 Fig. 8 depicts further the identification and investigation of functional group vibrations of
403 melanin and melanin: TiO₂ hybrid nanostructures with a more comprehensive spatial range
404 by using NICOLET 6700 Fourier Transform infrared spectroscopy (FTIR). The IR spectra
405 indicated clearly that the large absorption due to functional group of melanin and hybrid
406 melanin-TiO₂ nanostructures were characterized with different bonds in their respective regions
407 as depicted on top of Fig. 8. The peak values assigned to different modes of vibrations at 1150-
408 1371 due to C-C, C-O, and at 1460 cm⁻¹ due to C-N vibrations are similar to the reported values
409 in references [45]. A wide band centered at ~3000 cm⁻¹ in both spectra was observed, which is
410 corresponding to O-H stretching due to the presence of water in the melanin structure. IR
411 absorption peaks in the range of 1460- 1730 cm⁻¹ are assigned to the bonding vibrations of C=C,
412 C=O and to the stretching of COOH double bonds. Moreover, in the blend thin film (melanin:
413 TiO₂) the broad peaks observed at 3450-2400, 1609 and 720 cm⁻¹ were ascribed to the presence
414 of OH, C=O and Ti-O in the catalyst, and is suggesting the oxidative polymerization in the
415 formation of hybrid nanostructure [46].



416

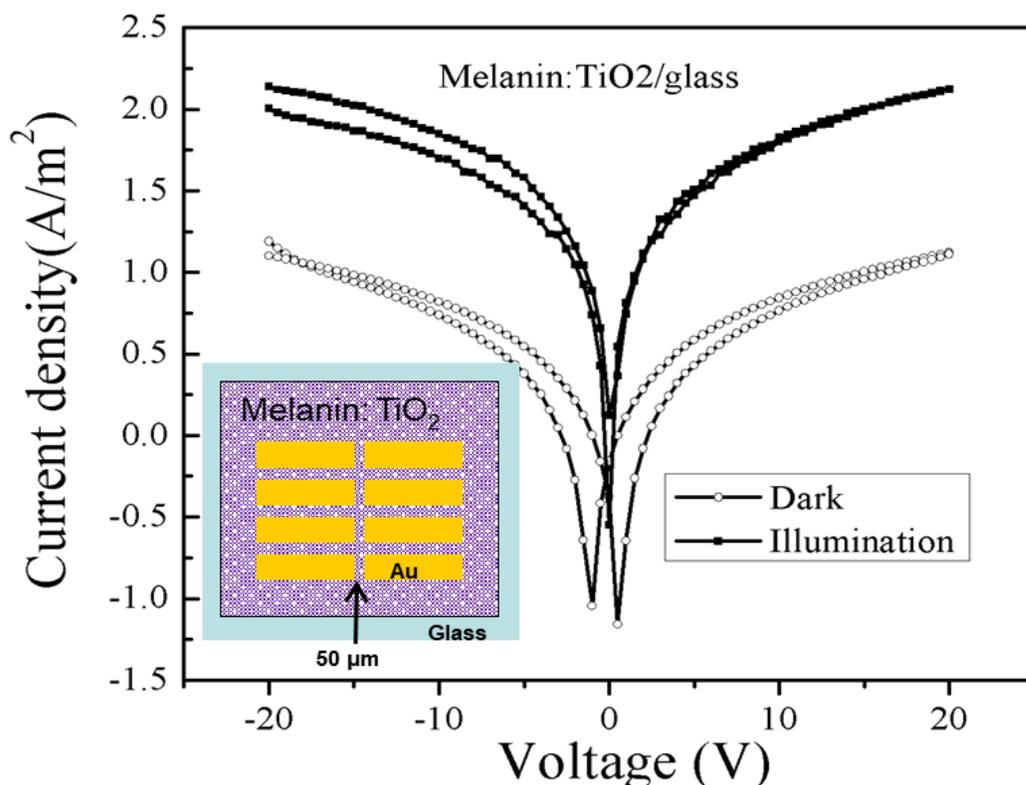
417 **Fig. 8.** IR absorption spectra of melanin thin films (lower-solid curve) and melanin: TiO₂ thin films
 418 (upper-dot curve) deposited by controlled ESD methods.

419 **3.5. Electrical characterization**

420 The charge transport characteristics of ESD synthetic melanin blended with TiO₂ nanoparticles
 421 films were measured under nitrogen- gas condition to avoid any surrounding effects. In Fig. 9 the
 422 Current–Voltage (J –V) curves were obtained by using a Keithley 4200 semiconductor analyzer
 423 in dark and under illumination of an AM1.5 (100 mW/cm²) calibrated with IL1400BL
 424 radiometer. Gold stripes were evaporated with a channel length of 50µm onto 7059 Corning
 425 glass substrates after film deposition to get planar geometry for J – V measurements in both
 426 forward and backward voltage sweep directions. In principle, more detailed analysis and
 427 improved performance could be obtained in the future by sandwiching the blended layer between
 428 two electrodes for an ideal devices modeling. At room temperature, the hysteretic behavior of
 429 melanin: TiO₂ films as shown in Fig. 9, contracted noticeably compared with hysteretic behavior
 430 that was reported in the previous work of ESD melanin films [6], due to the presence of shallow

431 trap states and to the existence of two types of water weakly and strongly bounded in melanin
432 pores structures [9,12].

433 Previously, it was described that the electrical transport across the melanin active layers could
434 strongly be affected by hydration state [3,5,9,12] Such effects in the J-V curve for hybrid
435 nanostructures layer were compensated by the presence of TiO₂ as an electron acceptor in the
436 melanin matrix by filling the pores structures, while in case of ESD melanin films these trapped
437 charges were released due to phonon-assisted hopping with increase in temperature. Moreover,
438 the photocatalytic and water splitting characteristics of TiO₂ played crucial role to alter the
439 hydration state for melanin charge transport mechanism in a reorganized structure. To assess the
440 photo response of such active layer for organic/inorganic solar cells, the J-V curves for melanin:
441 TiO₂ films under illumination were obtained. We found a strong photo response in the
442 photoactive layer of melanin: TiO₂ thin film. The resistance of ESD melanin: TiO₂ film is very
443 low at room temperature compared with ESD melanin films [9]. It is worth to note that TiO₂
444 nanoparticles as an electron acceptor semiconducting materials probably enhanced the charge
445 transport towards electrodes by the reduced charge recombination effect in the active layer when
446



447

448 **Fig. 9.** J-V curve of a planar blend (melanin: TiO₂) structure both in forward and backward voltage sweep
449 directions, measured by two Au electrodes separated by 50 μm. In the inset a planar geometry for J-V
450 measurements on glass is shown.

451
452 added with melanin. These results are in agreement with optical, morphological and structural
453 analysis, and revealed that hybrid melanin: TiO₂ nanostructures are active semiconducting agents
454 that can be employed as potential biocompatible nanomaterials in organic/inorganic bio/
455 (opto)electronic devices technology.

456

457 **4 Conclusions**

458 In this work, we described the formation of hybrid nanostructures of melanin with TiO₂
459 nanoparticles by ESD technique. Morphological analysis of the ESD thin films revealed quite
460 homogeneous and uniform flat surfaces covering the complete substrate area. **After subsequent**
461 **thermal annealing, the oligomeric aggregates characteristic of melanin, as well as the hybrid**
462 **nanostructures interfaces area are increased due to the mild distribution of titania particles in the**
463 **melanin matrix and the strong adhesion between them that strongly influenced the physico-**
464 **chemical properties.** The broadband absorption of the melanin: TiO₂ hybrid films also increased
465 as a result of the interaction of TiO₂ nanoparticles especially on the conducting substrates. In
466 fact, after heat treatments the absorption features in the optical absorption and PL characteristics
467 of melanin: TiO₂ layers on ITO substrates were enhanced. These facts preannounced the
468 reorganized growth mechanism of self-assembled supramolecular structures with increasing
469 degree of oligomerization and π-stacking of oligomers. In our opinion this result opens the way
470 to a possible tuning of the band gap values and increase in the External Quantum Efficiency
471 (EQE) in the infrared range of wavelengths. However, further quenching of the PL broad
472 emission peaks is still an open issue for experimental researchers to balance the charge carrier
473 mobility of optoelectronic devices with higher efficiency. These experimental results including:
474 efficient charge transport mechanism, rationalized feature of absorption and quenching of PL
475 emission, robust formation of melanin: TiO₂ hybrid nanostructures (elucidated by Raman and IR
476 spectroscopies), represent a significant step toward future implementations of optoelectronic and
477 bio-electronic/sensor devices using this important bio-polymer. .

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484

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Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

X The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Camerino 19/07/2020

Roberto Gunnella

A handwritten signature in black ink that reads "Roberto Gunnella". The signature is written in a cursive style with a large, stylized initial 'R'.