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On the origin of electrical conductivity in the bio-electronic material melanin

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The skin pigment melanin is one of a few bio-macromolecules that display electrical and photo-conductivity in the solid-state. A model for melanin charge transport based on amorphous semiconductivity has been widely accepted for 40 years. In this letter, we show that a central pillar in support of this hypothesis, namely experimental agreement with a hydrated dielectric model, is an artefact related to measurement geometry and non-equilibrium behaviour. Our results cast significant doubt on the validity of the amorphous semiconductor model and are a reminder of the difficulties of electrical measurements on low conductivity, disordered organic materials. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3688491]

The electrical properties of bio-molecules such as proteins and DNA have attracted significant scientific attention for several decades.[1–5] This interest stems from a desire to understand fundamental processes in biology and from the intriguing possibilities of using bio-molecules in electronics,[6] i.e., bioelectronics. The skin pigment eumelanin (hereafter referred to as melanin[7]) is one system that has recently emerged as a strong candidate for bioelectronics because of the advances in producing device-quality thin films[8–10] and the prevailing model that it is perhaps the only biological amorphous semiconductor.[7,11–16] A full model of charge transport in melanin has remained elusive for a number of reasons including (1) its electrical properties are very sensitive to hydration[9,16–20] and (2) there are difficulties associated with forming good ohmic contacts for accurate and reproducible measurements (due to surface roughness). These issues have led to observations of apparent n and/or p-type transport dependent upon experimental conditions,[19,21] anomalous Arrhenius behaviour,[9,13,16,18,22] dominant capacitative effects reminiscent of ionic materials,[17,18,20] and a general lack of agreement as to how electrically conductive melanin actually is.[7] In this letter, we report the first systematic and controlled study of the conductivity of melanin as a function of hydration (both in the dark and under illumination) with different electrical contact geometries. We show that a change in geometry leads to qualitatively and quantitatively different behaviour and that the traditional sandwich measurement architecture delivers misleading results.

Melanin has been described as a Mott-Davis amorphous semiconductor (MDAS) for over 40 years.[7] This model is based primarily on the work of McGinness et al., in which solid pellets of melanin were observed to switch between two resistive states by the application of an external voltage.[12] A peculiar feature of these experiments was that switching was only seen when the melanin samples were hydrated. To account for this, the MDAS model was rationalized in terms of a modified dielectric theory[12,17] according to

$$\sigma = \sigma_0 \exp\left(\frac{E_D}{2RT}\right)\exp\left(\frac{e^2}{2RTr}\left(\frac{1}{\kappa} - \frac{1}{\kappa'}\right)\right), \quad (1)$$

where σ is the conductivity, σ_0 is the dry conductivity in the infinite temperature limit, E_D is the energy gap of dry melanin, T is the temperature, r is the screening length, κ is the dielectric constant of dry melanin, and κ' is the effective dielectric constant of melanin due to the presence of water. Essentially, as water is added, the average dielectric constant increases leading to a reduction in the effective energy gap. This allows for the switching behaviour to emerge at voltages lower than breakdown.

The modified dielectric MDAS model appears to have support from two additional experiments measuring melanin conductivity as a function of hydration.[16,17] Although the methodologies for controlling hydration in these two studies were quite different, the experiments shared one feature—the use of the sandwich contact geometry (inset of Fig. 1(a)). We have previously reported the full water adsorption isotherms for solid melanin pellets made from pressed powder.[23] These isotherms demonstrated that long timescales (of order hours) are required to achieve equilibrium water content in the pellets. This led us to question the validity of the sandwich geometry given the dramatically reduced surface area available for water absorption and the relatively short timescales allowed for equilibration in the previous studies.[16,17] Based upon this insight, we redesigned the traditional sandwich geometry experiments under more carefully controlled conditions and also implemented "an open contact" geometry to ensure equilibrium hydration conditions via a surface van der Pauw (vdP) electrode architecture (inset of Fig. 1(b)). The latter four contact geometry has the significant advantage of exposing more surface area of the sample to the environment (∼71%, see supplementary information[27]) when compared to the sandwich configuration (∼37%).

Melanin was synthesised according to standard methodologies.[23,24] Briefly, a basic solution (pH 8) of dl-dopa was made and air bubbled through the solution for 3 days forming a precipitate. The solution was then brought to pH 2, the precipitate was filtered, washed with deionised water (Milli-

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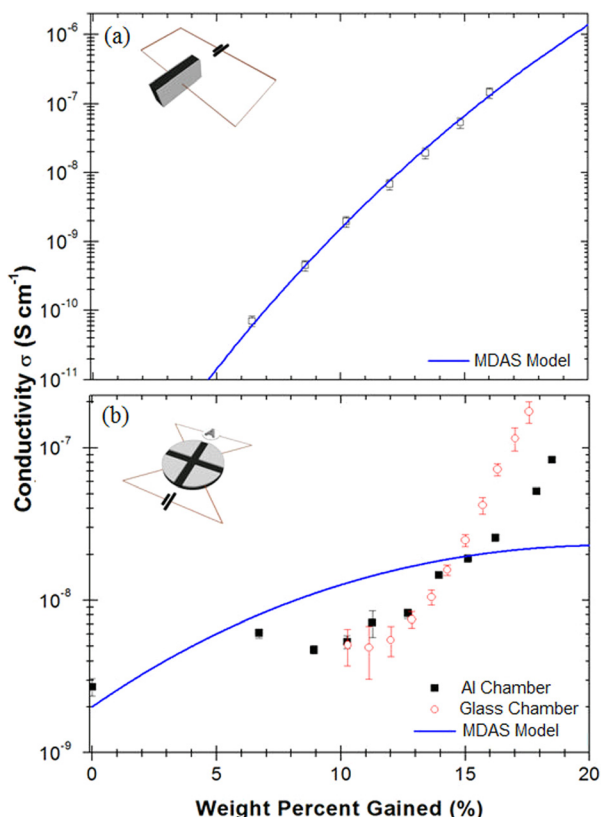
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FIG. 1. (Color online) Melanin conductivity vs. water content utilizing the sandwich geometry (a) and vdP geometry (b). The solid lines indicate the MDAS model prediction. Furthermore, contact geometries are indicated.

Q), and dried. The resultant powder was then pressed (10 t) into pellets. Sandwich samples were contacted by thermal evaporation of gold onto both faces of the pellet, out of which a rectangle was cut. Samples for the vdP geometry were contacted via evaporation through a shadow mask leaving 2 mm for an active channel and then mounted on a plastic sample holder with a hole so as to expose the non-contacted face. In both the experiments, wires were attached with silver paint and the samples placed within an aluminium vacuum chamber (see Fig. S1 (Ref. 27)) with a separate vapour system capable of delivering pure water vapour at a defined pressure. It is important to note that creating ohmic contacts using gold electrodes is troublesome due to diffusion of the metal into the pellet, the microscopic surface roughness, and carrier blocking at low hydration levels. The samples were hydrated by increasing the vapour pressure in 1.5 mbar–3 mbar increments, and the system allowed to reach partial or full equilibration for 1 h in a similar manner to our previous adsorption study.[23]

Current-voltage (IV) measurements were performed using a Keithley 2400 Source Meter Unit (SMU) under both dark and illuminated conditions. For the case of the sandwich geometry, brief details of the electrical measurements were as follows: (1) dark—a potential of 15 V was applied for around 50 s and subsequent current recorded and (2) illuminated—a white light source (spectrum Fig. S6) was switched on at time $t \approx 50$ s, and the sample illuminated for a further 50 s and the peak photocurrent recorded. For the vdP sample: (1) dark—a linear voltage sweep (in 4 terminal mode) was applied between -5 V and $+5$ V and the average

current measured and (2) illuminated—as per the sandwich geometry sample. Further details of the preparation, measurements, and data analysis are given in the supplementary information.[27]

The procedure was repeated up to a relative water vapour pressure of 0.8 ($\sim$21 mbar at room temperature). The water contents of the samples were determined using adsorption isotherms published previously.[23] Our measurement system was designed to alleviate two basic issues with the previous published experiments: (1) the problem of contamination arising from the use of salts to achieve set levels of environmental humidity[16] and (2) the improvement in signal-to-noise (S/N) afforded by using the aluminium chamber as a Faraday cage.[17]

The results of the sandwich geometry measurements are shown in Fig. 1(a). The qualitative behaviour is very similar to that reported previously[16,17] albeit with lower error and higher S/N—the conductivity increases by orders of magnitude in a sub-exponential manner. Critically, the data appears to fit the MDAS model (Eq. (1)) very well (as did Rosenberg and Powell's data[17]), although we note the fitting parameters are wholly unrealistic (see Table SI (Ref. 27)). This experiment at face-value agrees with the historical record.

The vdP geometry closely approximates the conditions under which previous adsorption isotherm studies established the equilibrium hydration time and water content.[23] Fig. 1(b) (Al chamber) shows the van der Pauw conductivity as a function of hydration which demonstrates a dramatic qualitative difference relative to the sandwich geometry. There are three distinct regimes in the "conductivity isotherm": an initial sharp increase up to $\sim$6.5 wt. %, a plateau up to $\sim$11 wt. %, and super-exponential behaviour up to maximum hydration. This data cannot be rationalised in terms of the MDAS model irrespective of the fitting parameters. It should be noted that we also performed the identical measurement in a glass chamber similar to Rosenberg and Powell[17] and obtained identical results to the Al chamber albeit with significantly increased noise (Glass chamber in Fig. 1(b) with data only accessible >10 wt. %).

We now turn to the photoconductivity data. Since illumination should produce an instantaneous change in conductivity, the magnitude of which depends upon the state of hydration, we should observe no qualitative differences between the two geometries. Furthermore, photoconductivity measurements have been used to justify the MDAS model.[14] Representative data for the sandwich configuration are presented in Figure 2 with additional data provided in Fig. S4. Qualitatively similar results were obtained for the vdP geometry (Fig. S5) although we note the lower currents (and hence lower S/N) generated for the same illumination intensity due to the differing field geometries. In all cases, after the initial application of a measurement voltage, a stable current level is attained (normalised as the zero photocurrent value). Illumination induces a photocurrent response which reaches a maximum value with a time constant of the order of seconds. Heating from strong nonradiative coupling of white light into the melanin samples[25,26] causes a reduction in water content and a subsequent increase in resistance—this effect is more pronounced at higher water content as expected from melanins' water binding capacity.[17,23] When the illumination
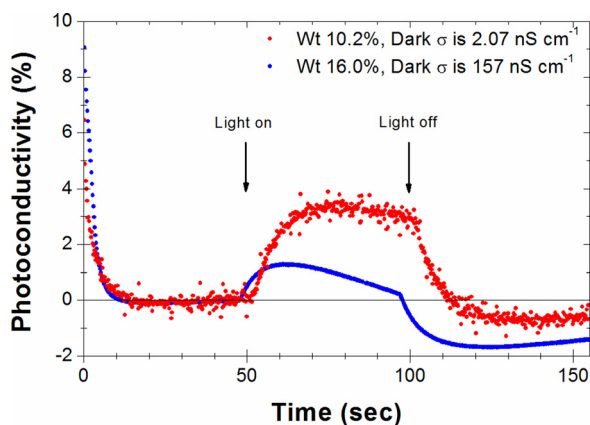
FIG. 2. (Color online) Two representative photoconductivity traces obtained using the sandwich geometry and a white light source illumination. The dark conductivity (initial equilibrium value pre-illumination), hydration level, and the light on/off points are indicated.

is removed, the photocurrent dissipates with a time constant again of the order of a few seconds and finally a new (lower—due to the reduced water content) equilibrium dark conductivity is re-established. The fact that heating and subsequent water desorption produces an apparent negative conductivity must be emphasised, since as mentioned earlier, it has been used to justify and strengthen the case for the MDAS model. Specifically, it was argued by Crippa *et al.*[14] that the negative conductivity was due to trap states in the photo-bandgap of melanin—a feature seen in amorphous semiconductors. The simpler explanation of heating induced water desorption emerges under careful environmental control and through a detailed knowledge of nonradiative conversion of absorbed photons,[25,26] and the adsorption,[23] and conductivity isotherms.

Taken together, these results, made using a carefully controlled dark/photoconductivity measurement protocol, show behaviour very different to that predicted by the MDAS model. We have demonstrated that the standard sandwich contact geometry for measuring the electrical properties of melanin has led to systematic errors in interpreting the charge transport behaviour. These errors arise due to non-equilibrium water adsorption behaviour—a feature that only emerges with an understanding of the relevant adsorption isotherms. A vdP contact geometry allows for equilibrium hydration to be established on a reasonable time scale and reveals the true conductivity versus water content behaviour of melanin. Analogous photoconductivity measurements confirm the findings from the dark measurements and reveal a simple explanation for negative conductivity—that is heating induced water desorption, not trapping/de-trapping in the melanin photo-bandgap. We, therefore, submit that there is no longer any reason for considering melanin an amorphous semiconductor, and a new model accounting for the domi-

nance of hydration is required. A more detailed analysis of the possible transport models consistent with our findings and reliable literature has been completed and will be reported elsewhere. This analysis strongly suggests that melanin is a hybrid ionic-electronic conductor which raises the intriguing possibility of using these materials as a bioelectronic interface. Finally, our study emphasises the difficulties in measuring the properties of low conductivity, moisture sensitive, disordered organic solids.

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[27]See supplementary material at http://dx.doi.org/10.1063/1.3688491 for more experimental and data analysis details.