Device-Quality Electrically Conducting Melanin Thin Films**

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Studying the optical and electronic properties of biological macromolecules has remained an active area of research during the last decade. In particular, electrical transport in DNA has been the subject of extensive investigation.[1,2] The condensed-phase electrical properties of proteins have also interested many, with groups even being able to produce a prototype protein-based field-effect transistor.[3,4] Melanin is an ubiquitous biological macromolecule that has been shown to possess intriguing condensed-phase physical properties.[5,6] These include electrical conductivity and photoconductivity as well as threshold and memory switching. Melanin is also known for its strong optical absorption that ranges from the ultraviolet (UV) to the near-infrared (NIR). These properties have been interpreted by many as evidence that melanin is an amorphous organic semiconductor.[7] Natural eumelanin is the most common form of melanin found in humans.[8] As a photo-protectant it strongly absorbs UV and visible light and then very efficiently dissipates the potentially damaging absorbed energy as heat.[9]

It is the manifestation of this combination of optical and electronic properties in a biological macromolecule that has drawn the attention of materials physicists to melanin. Synthetic eumelanin, which is generally accepted to be representative of natural eumelanin, is prepared by a standard procedure that involves the auto-oxidation of dihydroxyphenylanaline (dopa) to yield a melanin powder.[10] Owing to its insolubility in most common solvents, the melanin powder obtained in this manner cannot be easily processed with conventional polymer processing methods. This has meant that pellets made from compressed powder have been the only form of synthetic melanin available in the solid state. This practical difficulty has proven to be a near insurmountable obstacle that has long stood in the way of a detailed characterization of the material and the tantalizing possibility of incorporating melanin into electronic and optoelectronic devices.

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The production of continuous thin films from conventional synthetic melanin presents a significant step forward to overcoming this hurdle. These films are amenable to detailed electrical characterization (ac and dc) and also allow for carrier-type and mobility measurements through time-of-flight and related techniques. Thin films are also much easier to probe using condensed-phase optical spectroscopy. Being able to produce thin films underpins a whole range of these and other fundamental characterization techniques that are widely used in the field of organic electronics.

Thin films also form the basis for a number of different device configurations. These include chemi-sensors, next-generation solar cells, and a range of other detectors. A specific example of a device based on a melanin thin film would be a field-effect transistor with chemi-sensitive channel conductance. Melanin thin films also possess a number of physical properties that make them highly attractive for use in organic bioelectronic devices. As a biomaterial melanin is inherently biocompatible, which is a very important property of any viable organic bioelectronic material.[11] The potential also exists to use melanin films as an effective radiation sensitizer that could greatly improve the spectral range and efficiency of superconducting transition-edge bolometers.[12]

In this Communication we report upon the production and characterization of high-quality, structurally stable melanin thin films with electrical conductivities comparable to that of amorphous silicon. The film internal and surface morphologies were probed using scanning electron microscopy and atomic force microscopy, and found to be compact and smooth on the nanoscale. The solid-state absorption coefficients of these films were also measured (scattering free) and found to be between 10^7 and $10^6\,\mathrm{m}^{-1}$ across the ultraviolet, visible, and near-infrared. The production of electrically conducting device-quality melanin thin films represents the first step in using this biomaterial in organic electronic and optoelectronic applications, such as photon detection and chemi-sensing. Furthermore, these films are amenable to detailed physical and optical characterization, paving the way for deeper and more systematic fundamental studies of melanin structure–property relationships.

There have been previous reports of thin films produced from a melanin analogue compound that was engineered to be soluble in the organic solvents dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).[13,14] However, it has yet to be shown conclusively that it is a valid model system for melanin. Once this has been established, it would be interesting to

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compare the properties of films produced from the melanin analogue and conventional synthetic melanin.

The crucial step in the technique reported here for producing thin films from conventional synthetic melanin is being able to produce a melanin solution that can be spin-cast to produce films. In order to do this one needs to solubilize the melanin in a solution where all of the components other than the melanin will evaporate when it is cast. Conventional polymers are soluble in a range of volatile organic solvents, and therefore this does not pose a problem. However, melanin is notoriously insoluble and is only known to dissolve in strongly alkaline aqueous solutions. This property is believed to be a pH effect, related to the deprotonation of the various acid/base moieties found in melanin (which include carboxylic acid and phenol groups) that causes all of the components of the synthetic melanin to dissolve.[6] Normally, concentrated sodium hydroxide solutions are used to solubilize melanin. If these solutions are spin-cast the sodium hydroxide is deposited along with the melanin as the water evaporates. This means that even if a homogenous film could be produced from these solutions, it would contain significant amounts of sodium hydroxide as an impurity. Despite this fact, attempts have been made to produce homogenous films from melanin solutions containing sodium hydroxide, but none have succeeded. In the process here we use ammonium hydroxide as the base that is required to dissolve the melanin. When the ammonia and melanin solution is spin-cast the water evaporates along with the ammonia, leaving the synthetic melanin as a uniform film. Interestingly, natural melanin from *Sepia officinalis* has also been reported to be soluble in an ammonia solution.[15] This suggests that it may be possible to use this technique to produce thin films from biological melanin.

In order to probe the internal structure of the films and microscopic morphology, the films were examined using scanning electron microscopy (SEM). Figure 1 is a microscopy image showing one of the thicker films that has been lifted off the substrate in order to observe the cross-sectional profile. The figure shows that the top of the film has a smooth
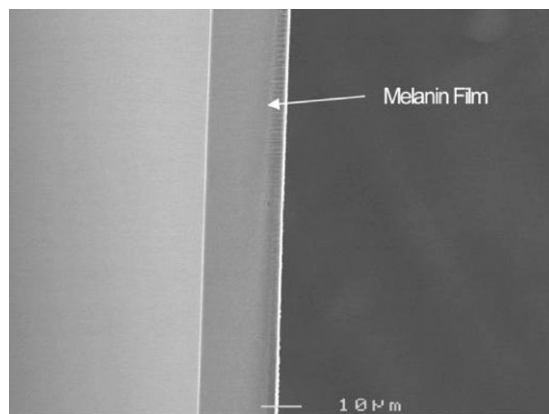

Figure 1. SEM image of the cross-section of a melanin film. The slightly ribbed structure at the back of the film is thought to be caused by lifting it off the substrate.

morphology. The cross-section shows that the film is dense and continuous, appearing free from voids or structural inhomogeneities. In order to probe the surface morphology of the melanin films a typical 430 nm thick film cast onto silicon was examined at a higher magnification by using atomic force microscopy (AFM).

Figure 2 shows AFM images of the surface of one of the films at different levels of magnification and a plot of how the root-mean-square (RMS) surface roughness of the images change as a function of image size. Figure 2a shows that even when the film area under observation is as large as $44 \times 44\,\mu m^2$ the RMS roughness is on the order of 1 nm. As the image size decreases this decreases evenly, to less than 0.6 nm when the scan area is $0.5 \times 0.5\,\mu m^2$. Figure 2b and c show reasonably large areas of the film covering $44 \times 44\,\mu m^2$ and $30 \times 30\,\mu m^2$, respectively. The film appears homogenous, being free from voids or cracks. There are several sharp protrusions on the images which are thought to be the result of dust on the sample. The films could not be prepared in a clean room and so some amount of dust contamination is inevitable. Even with these features the RMS roughness of both images is still approximately 1 nm, indicating that the films are homogenous and smooth on the micrometer scale.

Figure 2d through to f show increasingly higher-resolution images of the melanin film surface. As the resolution of the images increases, a nanoscale structure emerges on the surface of the film. Figure 2d is smooth and uniform but the film appears to be slightly granular. Figure 2e confirms that this granularity is not an artifact, and it appears that the film surface is composed of closely packed melanin spheroids that are on the order of tens of nanometers across. Figure 2f shows a higher-resolution image of the spherical particles, which appear to be around 20 nm in diameter.

In a four-terminal measurement, dc electrical conductivities were recorded for a typical melanin thin film. The conductivity proved to be strongly depended on the hydration state of the sample, a feature observed throughout the literature.[16] The film showed Ohmic behavior and had a conductivity of $\sigma = 2.5 \times 10^{-5}\,S\,cm^{-1}$ at a relative humidity of 100% and a temperature of 24 °C. Melanin is known to be able to strongly chelate a substantial amount of transition metal ions.[17] Even trace amounts of these have the potential to significantly affect the conductivity of the melanin films. To check that the films were not contaminated by metal ions or other contaminants an X-ray photoelectron spectroscopy (XPS) wide-scan survey spectrum was acquired for a melanin film. The spectrum showed a complete absence of any metals and the presence of carbon (61.1%), oxygen (22.6%), and nitrogen (15.3%), as expected. It also showed a trace amount of organic silicon (<1%), which is known to be a common polymer surface contaminant and would not have significantly influenced the electrical conductivity.[18]

Figure 3 shows the solid-state extinction coefficient of a melanin film as a function of wavelength. The plot shows that, much like melanin in solution, the absorption closely follows a decaying exponential in wavelength. The measured optical
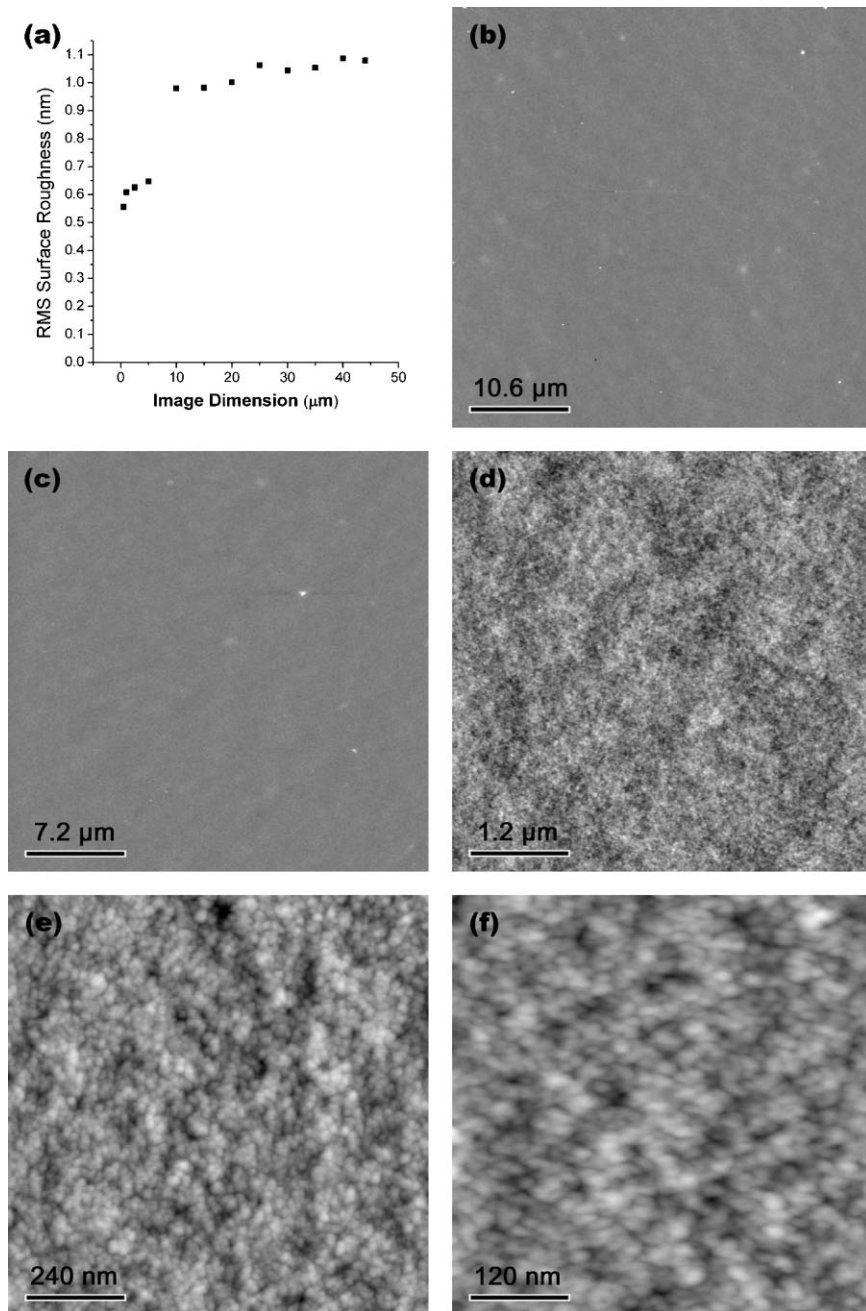
Figure 2. Tapping-mode AFM images of a 430 nm melanin film on a silicon substrate. a) RMS surface roughness as a function of image dimension. b) $44 \times 44 \, \mu m^2$ section, Z scale 50 nm. c) $30 \times 30 \, \mu m^2$ section, Z scale 50 nm. d) $5 \times 5 \, \mu m^2$ section, Z scale 6 nm. e) $1 \times 1 \, \mu m^2$ section, Z scale 5 nm. f) $0.5 \times 0.5 \, \mu m^2$ section, Z scale 5 nm.

spectrum presented in the earlier paper does not qualitatively resemble the well-established absorption spectrum of melanin in solution.[9] In the paper the absorbsion is essentially constant from 400 nm to 800 nm, whereas our absorption spectrum is very similar to what is normally observed in solution. This discrepancy could be explained by a saturation effect in the photopyroelectric spectroscopy, caused by the very high optical density in this region of the spectrum.

Film stability is a key issue when producing an actual device from these films. The melanin films were shown to have excellent thermal- and photostability and adhered very well to both glass and silicon substrates. The thermal stability of the melanin films was tested by performing a thermogravimetric analysis (TGA) on film scrapings and also by heating films on glass and silicon. Heating the native films to approximately 200 °C did not result in an observable change in film morphology, other than a decrease in thickness. The TGA revealed that at this temperature the film scrapings had lost less than 10% of their mass, which was undoubtedly a result of water loss. A 300 nm melanin film on glass was subjected to an extended photobleaching study by placing it under the illumination of a 150 W xenon lamp with UV filters at an illumination intensity of 100 mW cm^{-2} for 116 h of continuous illumination. After this time the absorption profile of the film remained virtually unchanged with a decrease of less than 1% in the absorbance across the visible spectrum. The film adhesion properties were tested following the standard procedure outlined by the International Organization for Standardization (ISO) for testing the adhesive properties of optical coatings (ISO 9211-4: the cross-hatch tape test – 100% pass).

absorption coefficient is approximately $3 \times 10^6 \, m^{-1}$ at 589 nm. This absorption coefficient is significantly larger than the value that has been reported for electropolymerized melanin that was measured using photopyroelectric spectroscopy.[19] The electopolymerized melanin has a very different morphology, showing a more open structure with cracks and voids that would reduce the overall density of the material and, hence, the absorbance. It is also curious that the absorption coefficient

In this Communication we have presented a simple fabrication process for the production of device-quality synthetic melanin thin films with electrical conductivity comparable to that of amorphous silicon. This presents a significant practical advance that will open the door to a range of characterization techniques and has the potential to shed new light on the fundamental physics at play in this intriguing biological macromolecule. It is also a crucial step toward
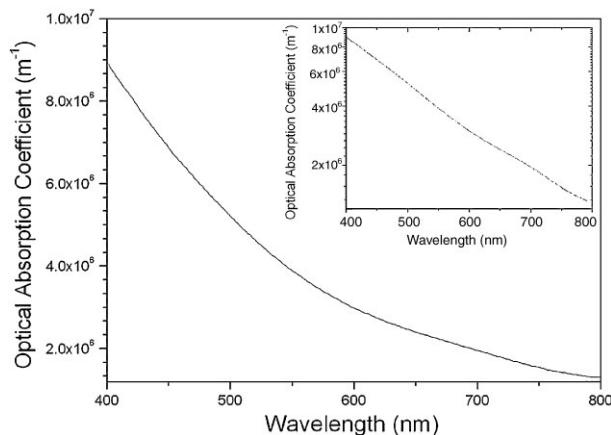
Figure 3. Solid-state extinction coefficient of melanin. The coefficient was determined from an absorption spectrum of a 400 nm thick melanin film by taking into account specular reflection and also scattering using an integrating sphere. The inset shows that on a logarithmic axis the extinction coefficient essentially varies linearly with wavelength.

harnessing melanin's optical and electronic properties in hitherto unrealized organic optoelectronic electrical devices. Additionally, these melanin thin films possess a number of highly desirable physical and biological properties that make them ideal for organic biolelectronic devices. It is also worth noting that, very recently, Lee et al.[20,21] have shown that melanin-like films produced from the polymerization of dopamine behave as multifunctional coatings and show quite remarkable adhesion to a variety of surfaces. These findings coupled with our results reported herein really underline the utility and potential of melanins as functional materials.

Experimental

Film Preparation: The stock solution that was used to prepare the films was made by adding synthetic eumelanin (700 mg) to a combination of water (5 mL) and concentrated ammonia solution (10 mL, 28%). The eumelanin was produced following the standard literature procedure outlined in Ref. [10]. The solution was then stirred at room temperature for 1 h and then ultrasonicated for a further hour to yield a pitch-black solution. In order to remove any particulates that would affect the film quality the solution was then centrifuged (3500 rpm, 15 min). The decanted supernatant formed the stock solution that was used to produce the melanin thin films. The thin films were made by simply spin-coating with the stock solution onto a glass or silicon substrate.

Electrical Conductivity: The electrical conductance of the films was measured in a four-point configuration using a Keithley 2400 SMU.

Surface Morphology: The surface morphology of the melanin films was investigated by scanning electron microscopy (6300F, JEOL) and atomic force microscopy (MultiMode SPM, Veeco). A MultiMode Scanning Probe Microscope working in tapping mode was used to obtain the AFM images. The film thicknesses were measured using a Dektak 150 profilometer.

Optical Absorption: Absorbance spectra were recorded using a Varian Cary 5000 UV-vis-NIR spectrophotometer. The specular and diffuse reflectance of thin film samples were measured with an integrating sphere using a custom-built Avantes spectrometer setup.

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