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Water-Based Melanin Multilayer Thin Films with Broadband UV Absorption

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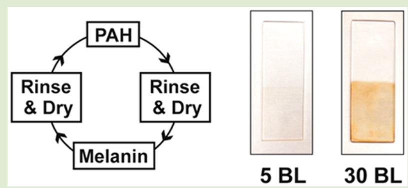
Supporting Information

ABSTRACT: Natural melanin is difficult to process due to its poor solubility and poorly understood structure. Synthetic melanin has been produced more recently, which is dispersible in mildly alkaline water and has many of the same properties of natural melanin. In this study, thin films of synthetic melanin and poly(allylamine hydrochloride) were deposited layer-by-layer from dilute aqueous solutions in ambient conditions. This is likely the first time melanin has been deposited from water to produce a functional nanocoating. These films display broadband UV light absorption, absorbing over 63% of incident light that is most damaging to human eyes with a thickness of 108 nm. In an effort to demonstrate the utility of these melanin-based nanocoatings, a 30 bilayer film is shown to increase the useful life of a conductive poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) film by 550%. This novel method of depositing melanin should open the door to a variety of useful applications.



Melanin is a widely available biocompatible polymer with many useful properties, such as semiconduction,[1] broadband UV absorption,[2−4] antioxidant behavior,[5] photoelectric behavior,[2] and free-radical scavenging.[5] In nature, melanin is responsible for the brown−black coloring in human pigmentation that protects the skin, hair, and eyes from the harmful effects of UV radiation.[2,3,6] Historically, melanin has been very difficult to adapt for broad use in materials applications because it is insoluble in all common solvents and usually exists as granular aggregates.[2,5] In an effort to expand its utility, recent research has focused on producing synthetic melanin, which is soluble in organic solvents.[5] Melanin thin films can now be produced by spin coating or drop casting.[7] A particularly useful synthetic melanin has been produced that is dispersible in mildly basic water,[5] allowing melanin to be processed without organic solvents.

Layer-by-layer (LbL) assembly is a powerful and versatile technique to deposit polymers, nanoparticles, or colloids from aqueous solutions to produce functional thin films which are typically no thicker than 1 μm.[8,9] These nanocoatings are most often deposited by alternately exposing a substrate to positively and negatively charged polyelectrolytes that are adsorbed as nanolayers, a pair of which is known as a bilayer (BL).[9] This technique has been used to produce thin films that are antiflammable,[10] impermeable to gases,[11] capable of purifying hydrogen,[12] antimicrobial,[13] superhydrophilic,[14] antireflective,[15] among many other useful properties. In this work, thin films of water-soluble synthetic melanin and poly(allylamine hydrochloride) (PAH) were fabricated via layer-by-layer assembly in ambient conditions from dilute aqueous solutions to produce extremely thin, well-adhered films with broad UV-protection capability. This appears to be the first time melanin has been deposited as a durable thin film from water using already-prepared melanin. These coatings absorb more than 63% of the UV light that is most damaging to human eyes (265−275 nm),[16] with a thickness of just 108 nm. Additionally, these films are shown to reduce UV damage to a thin conductive film of poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS). This novel method of producing melanin thin films could be useful for a number of applications requiring UV protection (e.g., eyewear, organic electronics, etc.).

Melanin-containing multilayer films were initially grown on silicon wafers and thickness was measured using ellipsometry and profilometry, as shown in Figure 2a. There is excellent agreement between these two measurement techniques. The PAH/melanin multilayer films grew linearly, depositing 1.7 nm per bilayer. The mass of the films was determined after each deposition step using a quartz crystal microbalance (QCM), as shown in Figure 2b, and the concentration of each component was calculated as described previously.[10,17] PAH/melanin multilayer films contain 37 wt % melanin and the melanin concentration is independent of the number of bilayers deposited. This is a significant increase over previous work, where only 5 wt % melanin was melt blended with common thermoplastic polymers that exhibited some visible melanin aggregation.[5]

Figure 3 shows the surface topography of these films in atomic force microscope (AFM) images. A five bilayer film

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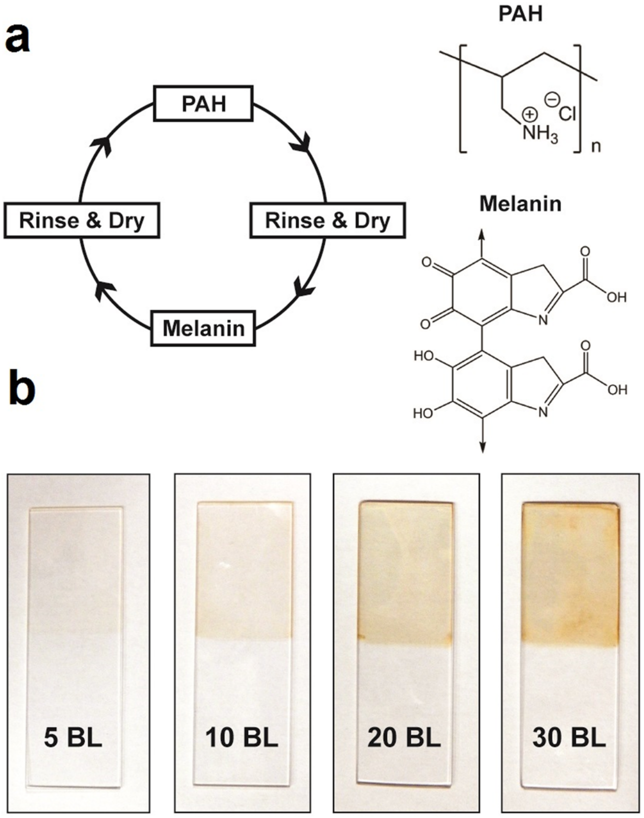

Figure 1. (a) Schematic of the layer-by-layer (LbL) deposition process and chemical structures of deposited polyelectrolytes. (b) Photographs of different numbers of PAH/melanin bilayers (BL) deposited on quartz.

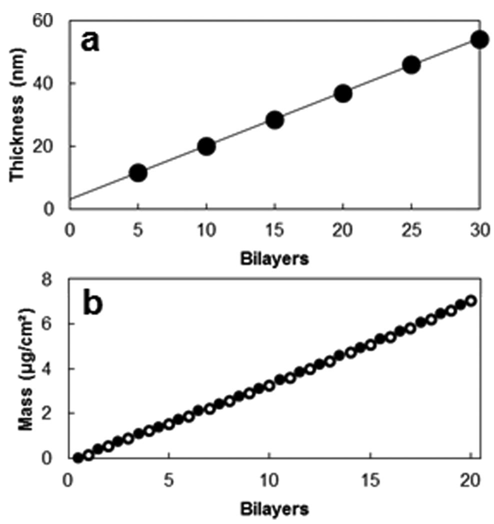

Figure 2. (a) Thickness of PAH/melanin multilayer films as a function of the number of bilayers deposited. (b) Mass deposited as a function of the number of layers deposited (filled points, PAH; open points, melanin).

deposited on quartz is composed of small islets on top of a thinner film (Figure 3a), which is likely an artifact of "island-growth" in the beginning stages of deposition. As the film grows, the roughness increases only modestly (R_a (5 BL) = 3.4 nm and R_a (30 BL) = 9.3 nm), suggesting that the film deposits in a uniform and coherent manner between 5 and 30 BL (rather than as semisolvated aggregates).[18] Previous work on

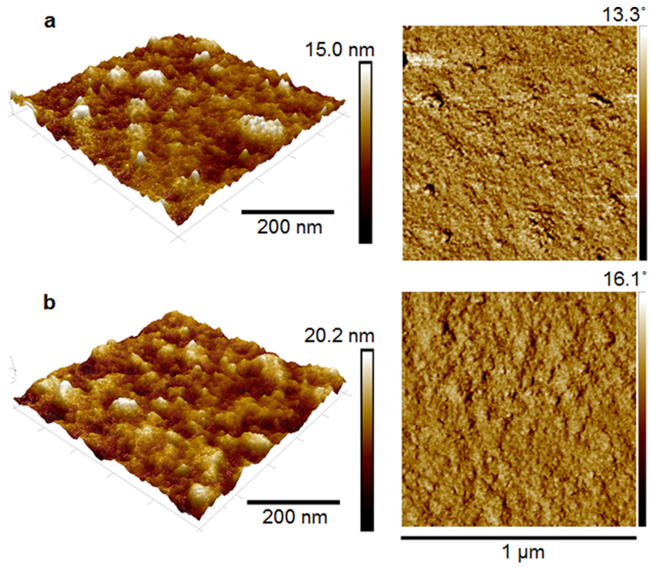

Figure 3. AFM 3D height and phase images of (a) 5 BL and (b) 30 BL PAH/melanin multilayer films deposited on quartz.

melanin thin films spin-coated from DMSO reported a surface roughness less than 0.4 nm at a film thickness of 30 nm.[19] It is believed that the low surface roughness of the spin-coated melanin film is due to self-arrangement of the melanin during solvent evaporation.[19] The electrostatic forces between the PAH and the melanin in the layer-by-layer assembled films likely prevent the melanin from rearranging into a smoother film, thereby locking in the island topography of the initial bilayers.

Melanin multilayer films on quartz display broadband UV−vis light absorption from 200−700 nm, as shown in Figure 4a. Vertebrates use melanin to prevent eye damage from short wavelength UV light, particularly from 265−275 nm,[6,16,20,21] and a quartz substrate coated with a 30 BL melanin-containing multilayer film on both sides absorbed 63% of the light in this range. As a comparison, neat melanin and PAH were spin coated onto quartz from water. The multilayer films have optical properties very similar to natural melanin, displaying a broad absorbance of UV and visible light, which decreases slightly at higher wavelengths (Figure 4a).[2,4,22] Spin-coated melanin films display an additional peak at 280 nm, which is most likely due to the quinone in the melanin backbone (Figure 1a) reverting to a catechol under ambient conditions.[23] It is interesting to note that the backbone quinone melanin in the multilayer film did not revert back to a catechol in dry conditions, which may be due to interactions between the amine of the PAH and the quinone.

The absorbance spectrum of the melanin multilayer film is atypical of an organic chromophore and would typically be associated with scattering effects due to aggregated particles in the film.[2] It should be noted that melanin is known to display this broadband absorption curve even when well-solvated and, combined with the nature of the deposition method, is consistent with well-dispersed melanin in the multilayer film.[22] Figure 4b shows that the absorbance of the PAH/melanin films at various wavelengths of UV light is directly proportional to their thickness. This is further evidence that the melanin concentration of the film remains constant with increasing bilayers. Despite the multilayer film being only 37 wt % melanin, as determined by QCM, the total absorbance of the

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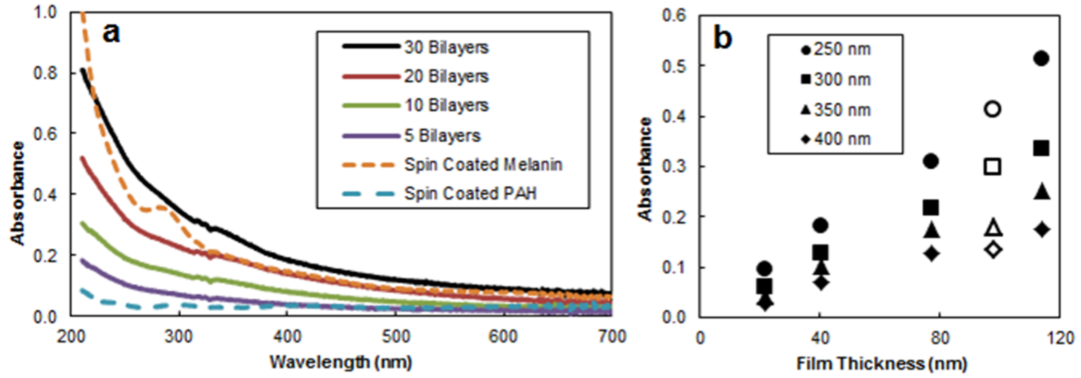

Figure 4. (a) Absorbance spectra of varying bilayers of PAH/melanin multilayer films, along with 98 nm spin coatings of the constituent polyelectrolytes on fused quartz. (b) Absorbance of the multilayer films (filled points) and spin-coated pure melanin films (open points) as a function of film thickness.

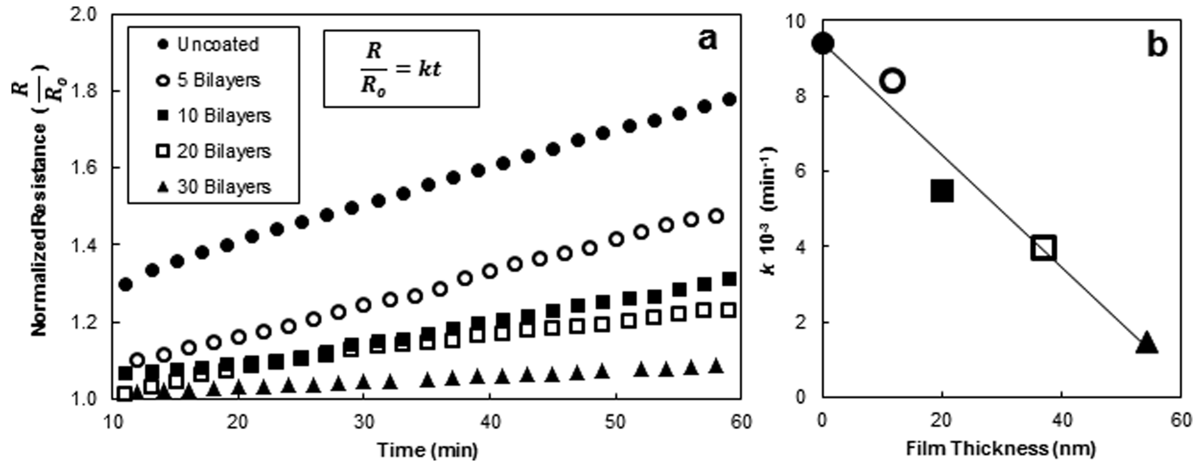

Figure 5. (a) Resistance of spin-coated PEDOT/PSS films coated with PAH/melanin multilayer films as a function of time exposed to UV light, and (b) the associated slope of the resistance as a function of PAH/melanin multilayer film thickness.

film is remarkably similar to a spin coated film composed entirely of melanin of similar thickness (Figure 4b). As the UV absorbance of the film is primarily derived from the melanin content, it is possible that the total melanin content is similar between the spin-coated and LbL films, despite the additional PAH in the LbL film. It is well established that the conformation of the polyelectrolytes in LbL-assembled films allows for very dense films, exceeding the densities of the individual components.[12,17,24]

UV absorbance and antioxidant properties of melanin are well-established,[2] so PAH/melanin multilayer thin films were deposited on spin-coated PEDOT/PSS films to impart UV protection. PEDOT/PSS films were exposed to a 400 W mercury arc lamp, which degraded the film over time. The increase in electrical resistance was used to monitor PEDOT degradation, as shown in Figure 5. Uncoated PEDOT/PSS quickly degrades in UV light,[25,26] becoming 80% more resistive after 1 h of exposure (Figure 5a). The degradation of the film initially increased rapidly, but approached steady state after 10 min, after which the resistance increased linearly with time. This increase in resistance of the PEDOT/PSS is due to overoxidation, which causes chain scission and reduces π transitions of the PEDOT.[24] The UV damage to the PEDOT was significantly reduced when the melanin multilayer film was added on top. With 30 bilayers, the longevity of the PEDOT increased by 550%. Figure 5b shows the decrease in UV damage is directly proportional to the thickness of the multilayer film. The melanin-based multilayer film itself is not conductive, but only marginally decreased the conductivity of the underlying PEDOT. These same nanocoatings could eventually be used as environmentally friendly organic semiconductors, free radical scavengers, or antifouling layers.

■ ASSOCIATED CONTENT

Supporting Information

Details of the experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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