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Operando Spectro-electrochemical Characterization of Melanin

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Abstract

Traditional approaches to establish structure-function relationships for materials rely on bottom-up chemical methods, but these approaches have been less successful for characterizing melanins because of the complexities associated with melanin's synthesis and molecular structure. In the absence of relevant molecular-level information, is has also been difficult to establish structure-function relationship through top-down measurements of melanin's properties (e.g., conductivity). Recently-developed "operando" methods for characterizing electronic materials partially bridge bottom-up and top-down approaches by simultaneously observing molecular-level changes while electron transfer processes are occurring (i.e., while the material is "in operation").

Here, we prepared a semi-transparent hydrogel film from a soluble melanin obtained from the black soldier fly (BSF) and applied operando spectroelectrochemical methods to investigate the molecular level changes that occur when electrons are "flowing" through this melanin. We observed that BSF-melanin is reversibly redox-active in the mid-physiological redox potential range which is similar to other melanins. We also observed electron transfer through indirect (mediator-based) mechanisms, and through a direct mechanism with conducting graphene. In both mechanisms, we show that electron transfer is correlated to a reversible switching of melanin's redox state. We believe that the direct ET between graphene and BSF-melanin likely involves an extrinsic electron transfer mechanism involving exchange between π-electrons of graphene and melanin. Interestingly, the redox-state switching observed during direct ET indicates that the electrons transferred from graphene to melanin do not necessarily continue "flowing" through the melanin but can be stored in a relatively stable redox state (presumably a reduced catechol state).

Finally, we provide evidence for a chemical disorder model in which the properties of melanin are the result of contributions from diverse structural and mechanistic features that occur over various length scales. Observations that support the chemical disorder model are: (i) the cyclic voltammogram has a "featureless" shape which suggests that direct electron transfer to BSF melanin involves multiple redox-active moieties with overlapping redox potentials; (ii) the redox differential absorbance broadened with increasing BSF-melanin content suggesting emergent interactions between different moieties; and (iii) the redox differential absorbance spectra depends

on the rate of redox-switching which suggests that the BSF melanin may have redox-active moieties that can be switched under slightly different conditions.

Overall, we show that operando spectroelectrochemical measurements can bridge traditional bottom-up and top-down methods to facilitate the characterization of melanin.