The Redox Behavior of DHI-Melanins

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Melanins are nature's ubiquitous black, catecholic pigments, which are thought to act as buffers against oxidative and photochemical stress. They are colloidal, heterogeneous polymers that are difficult to study via solution-based methods. To directly measure the chromophore's redox reactivity, we have formed synthetic melanoid films on electrode surfaces by oxidative polymerization of dihydroxyindole (DHI) precursors. These poly-DHI electrodes are used to model biologically important reactions of melanins in vivo.

Spectroelectrochemical titrations of poly-DHI films on optically transparent indium-tin oxide electrodes were used to characterize a reversible oxidation (forming quinone-imine subunits) and irreversible bleaching; the stoichiometries of these reactions were assayed by coulometry. The presence of oxygen during oxidation results in a competitive bleaching, forming peroxide, which may be attributed to reaction with semiquinone radical subunits.

Films pretreated with Cu and Zn salts show altered behavior, due complexation by oxidized quinone-imine subunits. LDI-MS, EPR and solution-based potentiometric titration experiments were used to correlate the speciation of metal complexation and redox behavior.