Electrochemical Synthesis in Microemulsions with Crosslinked Poly(L-lysine)-Protein Films

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Microemulsions are thermodynamically stable, macroscopically homogeneous mixtures of oil, water and surfactants with dynamic internal nanostructures capable of solubilizing polar, nonpolar and ionic reactants. Mediated electrochemical synthesis in microemulsions provides an attractive approach to environmentally benign organic synthesis, avoiding toxic, expensive organic solvents, and often accessing unique pathway control. We have reported various synthetic applications of metallopolyion catalyst networks covalently bound to electrodes that have good stability in microemulsions.

Biocatalysis promises to be a major facilitator of future chiral synthetic routes, since enzyme-catalyzed processes can be highly stereo- and regio-selective, efficient, and economical. In this paper, we address exploratory studies on the development of metalloheme protein films crosslinked with poly(L-lysine) on carbon electrodes designed for electrochemical synthesis in microemulsions. Voltammetry was used to examine the best method of film construction for stability in microemulsions and in presence of hydrogen peroxide, which is important for olefin epoxidations. Films of myoglobin (Mb) prepared layer-by-layer with poly(L-lysine) (PLL) and crosslinked at each bilayer step produced films that gave stable cyclic voltammetry in CTAB microemulsions for 10 hrs with up to 10 mM hydrogen peroxide present. Absorption and circular dichroism spectroscopy were consisted with Mb retaining a near-native secondary structure in these films.

Crosslinked Mb-PLL films on carbon cloth electrodes in simple stirred batch reactors gave turnover rates for the epoxidation of styrene up to 200-fold larger in bicontinuous CTAB microemulsions than in styrene emulsion in aqueous buffers, and about 130-fold larger than in micellar solutions of CTAB. This reaction involves catalytic activation of the ferric heme of Mb via electrochemical catalytic production of hydrogen peroxide. The protein is thereby converted to an oxyferryl species, which is the active oxidant. The reaction can also be driven by addition of hydrogen peroxide, which in CTAB microemulsions employing crosslinked Mb-PLL films gave comparable turnover rates to electrolysis. The enhanced reaction rate in bicontinuous microemulsions is consistent with a much greater availability of the reactant styrene compared to emulsions or micelles, in which most of the styrene is contained in slow-moving droplets.

A second system being studied involves films of cobalt-reconstituted myoglobin (CoMb) and PLL. The use of CoMb may allow us to access carbon-carbon bond formation analogous to vitamin B12. The most stable and active films were obtained by mixing CoMb and PLL, then crosslinking them on a carbon cloth electrode. Such films gave absorption and circular dichroism spectra consistent with a native protein structure, and square wave voltammetry revealed reversible peaks for the key catalytic Co(II)/Co(I) redox couple in CTAB microemulsions. Voltammetry confirmed the occurrence of key bond-forming catalytic reactions. The synthetic performance of these films in microemulsions will be discussed.