Direct electrochemistry and Spectroelectrochemical Studies of Myoglobin Encapsulated in Sol-Gel and Single-Wall Carbon Nanotube Thin Films.

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Electrochemical properties of heme proteins and enzymes have been a focus of many biochemical, electrochemical and spectroscopic research owing to their important role in the redox processes in biological system. Unfortunately, most of these proteins show a poor electrochemical behavior at the bare electrode surface. Film electrodes and chemically modified electrodes have been used to facilitate the electron transfer between the heme protein and electrode. In this study, the electrochemical behavior of myoglobin in various substrates including sol-gel matrix, single-wall carbon nanotube (SWNT) as well as surfactant film, Nafion, poly (vinyl alcohol) (PVA) film and silver nanoparticles have been investigated. The electrochemistry of Mb encapsulated in the sol-gel matrix is reported for the first time. It is found that the redox behavior of myoglobin varies from substrate to substrate. For example, the observed redox potential of myoglobin (Mb) in both sol-gel matrix and thin single-wall carbon nanotubes (SWNT) film on the glassy carbon (GC) electrode was approximately -250 mV (vs. Ag/AgCl in pH 7 phosphate buffer) which differs from those in dodecyldimehtylammonium bromide (DDAB) film (-200 mV) and Nafion film (-340 mV), while redox peaks are barely seen in PVA film. These myoglobin film electrodes also showed different catalytic properties of oxygen reductions. Spectroscopic methods including Resonance Raman and FT-IR and UV-Vis are employed to uncover the structural feature that can interpret the varied electrochemical properties. Raman spectroscopic results indicate that substrates may induce a structural change at the heme active site both at the proximal and the distal sides, as evidenced by the changes in relative intensities and positions of the bands at 340/370 cm^{-1}, and 1480-1640 cm^{-1} spectrum region. Resonance Raman, UV-Vis and FT-IR spectra indicated that Mb on the SWNT film retained a near-native secondary structure. These results were used to account for the electron transfer and catalytic properties of myoglobin in these matrices.

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