**Supramolecular electrode assemblies in bioelectrochemistry**

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For more than three decades, the field of bioelectrochemistry has provided novel insights into the catalytic mechanisms of enzymes, the principles that govern biological electron transfer, and has elucidated the basic principles for bioelectrocatalytic systems. Progress in biochemistry, bionanotechnology, and our ever increasing ability to control the chemistry and structure of electrode surfaces has enabled the study of ever more complex systems with bioelectrochemistry. In this tutorial lecture, I will highlights developments over the last one to two decades, where supramolecular approaches have been employed to develop electrode assemblies that increase enzyme loading on the electrode or create more biocompatible environments.

Supramolecular chemistry is concerned with systems that are comprised of molecular units that are assembled by weak interactions; they are primarily focused on electrostatic, van der Waals and hydrophobic interactions, and, more recently, metal coordination chemistry. Several approaches are highlighted in this lecture: (1) Supramolecular approaches to accommodate integral membrane enzymes; (2) The use of nano- and meso-porous electrodes or co-assemble of nanoparticles to enhance electroactive surface areas of electrodes; and (3) the use of layer-by-layer assembly.

Many redox enzymes are oxidoreductases and an important group of them reside in bacterial, mitochondrial or chloroplast (inner) membranes. Although many approaches have been developed to study and utilize redox proteins and enzymes in bioelectrochemistry, significantly less strategies have been developed for membrane proteins compared to globular proteins. Here, I will provide a brief overview of the strategies used to make electrodes suitable for membrane proteins.

The electrochemical surface area of electrodes can be greatly enhanced if either the electrode is structured or modified with length scales comparable to that of the redox proteins. Several key examples will be covered in this tutorial lecture, including mesostructured electrodes (although these are not strictly supramolecular approaches) and electrodes modified with carbon nanotubes and gold nanoparticles.

Finally, Layer-by-Layer (LbL) deposition has the ability to either increase enzyme loading on the electrode or to create well organized layers consisting of different enzymes that work in tandem in multistep reactions. For bioelectrochemical applications, the LbL systems either have to be permeable to electron mediators, which can be proteins, or the LbL system has to be conductive.

References:

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