Development and Characterization of Highly Efficient Integrated Bioelectrocatalytic Systems utilizing Nanostructured Carbon, Enzymes, Biofilms and Metal Nanoparticles

Pawel J. Kulesza

Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland

In our research we have exploited unique electronic and mechanical characteristics of multi-walled carbon nanotubes (MCNTs) to construct the efficient anodic and cathodic bioelectrocatalytic systems for biofuel cell applications. To stabilize composite films, we utilize MCNTs modified with ultra-thin layers of organic (e.g. 4-(pyrrole-1-yl) benzoic acid. We expect here attractive electrostatic interactions between anionic adsorbates and positively charged domains of the enzymatic sites. We have also utilized metalloporphyrin redox centers and such an enzyme as horseradish peroxidase (HRP) or cabbage peroxidase (CP). Co-existence of the above components leads to synergistic effect that is evident from some positive shift of the oxygen reduction voltammetric potentials and significant increase of voltammetric currents. The film has also exhibited relatively higher activity towards reduction of hydrogen peroxide. It is reasonable to expect that the reduction of oxygen is initiated at cobalt porphyrin redox centers, and the undesirable hydrogen peroxide intermediate is further reduced at HRP or CP enzymatic sites.

The development of bioanode has also been investigated. To facilitate electron transfer between the electrode surface and the redox protein centers, the concept of co-deposition of MCNTs within the bio-electrocatalytic film has also been pursued here. First, MCNTs have been modified with ultra-thin layers of tetrathiafulvalene (TTF). The presence of TTF is expected to facilitate an effective flow of electrons from the redox centers of glucose oxidase to the glassy carbon electrode. As before, MCNTs have supported transport of electrons within the bio-electrocatalytic film. Our highly MCNT-based porous films have presumably acted as 3D-network of nanowires around the enzyme molecules and have promoted the efficient electron transfers. Thus we have produced a catalytic system capable of effective oxidation of glucose.

In our research, we have exploited unique interactions of gold, silver and related bimetallic nanoparticles with biofilms formed by *Pseudomonas aeruginosa, Staphylococcus aureus and Yersinia enterocolitic* bacteria on glassy carbon electrodes. We consider here noble metal nanoparticles modified and stabilized with ultra-thin films of inorganic species (e.g. polyanions). Regardless the general tendency of gold and silver nanoparticles (suspended in aqueous solutions) to minimize formation of biofilms on solid surfaces, once immobilized within porous conducting polymer (e.g. poly(3,4-ethylenodioxythiophene) or PEDOT) layers, they tended to facilitate growth of robust and mature bacterial biofilms on their surfaces. Independent diagnostic electroanalytical experiments showed that biofilms grown by the following bacteria, *P. aeruginosa ATCC 9027, Y. enterocolitica Ye9, Y. enterocolitica AR4, L. monocytogenes 10403S* and *L. monocytogenes 1115*, on inert carbon substrates exhibited by themselves electrocatalytic properties towards oxygen and hydrogen peroxide reductions in neutral media. The processes were found to be further enhanced by introduction of certain metallic (Au, Ag, Pd) and bi-metallic (Au-Pt) nanoparticles both unsupported and supported on such inert metal oxide nanostructures as TiO_2 and ZrO_2. Coexistence of the above components leads to synergistic effect that is evident from some positive shift of the oxygen reduction voltammetric potentials and significant increase of voltammetric currents. Further, the proposed hybrid films exhibited relatively higher activities towards reduction of hydrogen peroxide. Comparative measurements were performed aiming at better understanding of electrocatalytic efficiencies of various systems including those utilizing metal nanoparticles (e.g. Au-Pt), conventional enzymes (e.g. laccase), molecular systems (e.g. metalloporphyrins) in the presence and absence of selected bacterial biofilms.