New metal-oxide electrodes for fast direct electron transfer to the redox proteins

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The direct, fast and sustainable electron exchange between redox proteins and electrodes is needed for the development of biosensors and electroenzymatic syntheses. Tin and indium oxide have been used for sustained electron transfer to redox proteins, however charge transfer rates were lower than using modified metal electrodes.Our goal was to show that such exchange is achievable on semiconducting metal oxide electrodes when their electronic properties are tuned to optimize electron transfer with specific proteins. Heavily doped cadmium tin oxide (CTO) film electrodes were prepared using simple sol-gel procedure. Their doping level and flat band potential were determined from Mott-Schottky plots. The nearly reversible direct electron transfer was demonstrated for the [2Fe-2S] proteins spinach ferredoxin (Sp fd) and Putidaredoxin (Pdx), and the well-studied

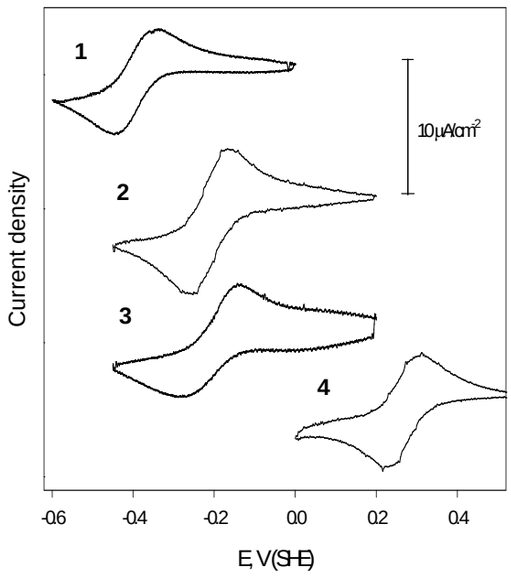

Fig 1. CV curves of several redox proteins measured on CTO electrodes. 1-Spfd, 2, 3-Pdx, 4-Cyt C.

heme protein horse heart cytochrome c (cyt c). These represent a family of proteins that are of comparable size, but vary significantly in overall charge, formal potential, and type of metal center. Annealing temperature and duration varied film properties, such as charge carrier concentration and flat band potential. The rates of electron transfer for the two ferredoxins obtained on these CTO electrodes are higher than the ones achieved at chemically modified metal electrodes.

Spectral measurements in a thin layer cell confirmed reversible protein active center reduction and the absence of denaturation.

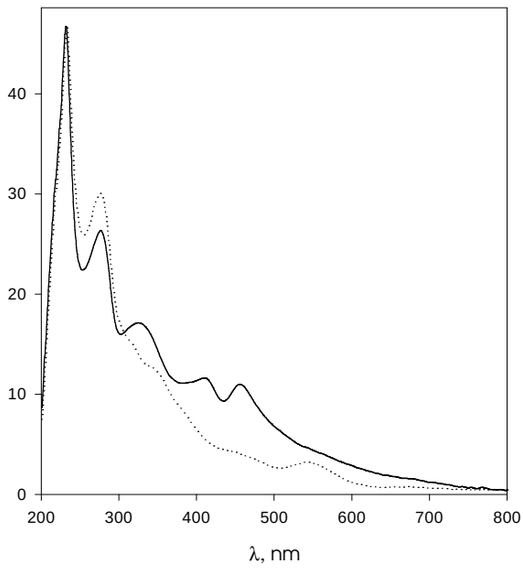

Fig.2 Absorption spectra of Pdx in a thin layer cell. Full line-oxidized, dotted line-reduced using metal oxide electrodes

Feasibility of these electrodes for a wide range of redox biomolecule studies is demonstrated. In conclusion, we have shown that heavily doped metal oxide materials can be superior to modified metal electrodes for sustained unmediated redox protein cycling.