Electrochemical Analysis of Homocysteine-Bridged Superoxide Dismutase Self-Assembled Monolayer Electrode

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Superoxide dismutase (SOD) has peroxidase activity in several free radical mediated inflammatory disorders. We have developed an SOD-modified electrode to study the electron transfer of SOD, in which SOD is oriented on the gold electrode via a self-assembled monolayer of homocysteine (Hcy-SAM) by 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). Cyclic voltammetry (CV) was used to study electrochemical behaviors of this SOD modified Hcy-SAM electrode (SOD-Hcy-SAM) in phosphate buffer solution. A pair of well-defined electrochemical redox waves of SOD were achieved compared with negative controls using bare gold electrode and solely Hcy-SAM modified electrode. SOD was found to be stably confined on Hcy-SAM with stable redox response suggesting permanent binding of SOD via the SAM bridge of Hcy to the electrode surface. The redox peak current increased with sweep rate as well as the ratio of oxidation to reduction peaks was not equal to 1, which demonstrated a quasi-reversible electrochemical behavior. Therefore, Hcy is an effective promoter for electron transfer by facilitating and speeding up the electron transfer of SOD. Hydrogen peroxide turnover by SOD weakened the electrochemical reversibility of SOD. The CV reduction peak current under -0.1 - 0.7 V sweep in pH 7.0 phosphate buffer was observed to decrease distinctly until disappear with the concentration of hydrogen peroxide increase, which indicated the decrease of SOD electron transfer by reduction of Cu complex moiety from Cu(II)SOD to Cu(I)SOD. The Cu complex moiety is supposed to be the electroactive site of SOD with inherent enzymatic activity for dismutation of superoxide ion. The decrease of SOD electron transfer further weakens the bridge between SOD and Hcy-SAM. This work was supported by Natural Science Foundation of Shandong Province Y2000BO3, P. R. China

Figure 1 Cyclic voltammetry diagram of SOD-Hcy-SAM in phosphate buffer. Scan rate 10, 50, 100, 150 mV/s from inside.