PHOTOELECTROCHEMICAL CHOLESTEROL BIOSENSING VIA P(SNS-NH_2)/CHOX/$[RU(BPY)_3]^{2+}$ MODIFIED ELECTRODES

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ABSTRACT

Despite the numerous studies on photochemically induced electron transfer in proteins[1], there is no precedence for the photonic wiring of redox enzymes with electrodes and their bioelectrocatalytic activation. The use of enzymes in fuel-generating solar cells has been discussed previously[2]. The electrical wiring of the enzymes in these systems was achieved, however, by applying natural cofactors (nicotinamide adenine dinucleotide (phosphate)) and their regeneration by photochemical means[3]. Also, the field of enzyme-based biofuel cells has been substantially advanced in the past decade, and numerous organic materials, such as alcohols, sugars, or a-hydroxy acids, have been used as fuels for the biocatalyzed generation of electrical power in the presence of oxygen (O_2) as oxidizer. In this study, a novel approach for constructing different very sensitive and efficient photoelectrochemical biosensors called as P(SNS-NH_2)/ChOx/$[Ru(bpy)_3]^{2+}$ and ChOx/$[Ru(bpy)_3]^{2+}$, were fabricated by bonding ChOx covalently to P(SNS-NH_2) modified electrode and bare thioaniline modififed gold slide respectively, using gluteraldehyde and tethering the N-hydroxy succinimidyl ester functionalized Ru(II)-trisbipryridine to the ChOx enzyme. In the presence of different concentrations of cholesterol, the photocurrents were obtained by irradiating of the photoelectrochemical cell containing P(SNS-NH_2)/ChOx/$[Ru(bpy)_3]^{2+}$ or ChOx/$[Ru(bpy)_3]^{2+}$ electrode as the anode under air. The bipyridine complex $[Ru(bpy)_3]^{2+}$ was used to activate photoinduced electron-transfer reaction and it acted as a redox mediator to activate the bioelectrocatalytic functions of ChOx. Therefore, it was shown the photonic electron-transfer wiring of ChOx with the electrode. ChOx/$[Ru(bpy)_3]^{2+}$ and P(SNS-NH_2)/ChOx/$[Ru(bpy)_3]^{2+}$ biosensors showed a very good linearity between 0.05-0.9 mM and 0.00625-0.6 mM for cholesterol respective. LOD values for P(SNS-NH_2)/ChOx/$[Ru(bpy)_3]^{2+}$ and ChOx/$[Ru(bpy)_3]^{2+}$ electrodes were obtained as $9.86x10^{-5}$ mM and $3.48x10^{-4}$ mM cholesterol respectively according to S/N = 3 ratios. Kinetic parameters, such as Km and Imax operational and storage stabilities, effects of pH and temperature were determined for both enzyme electrodes.

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