Directed Immobilization of a Heme Protein on Nanostructured Electrodes

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We show that directed immobilization of proteins/enzymes on electrode surfaces has the advantages of favorably tuning the direct electron transfer and electrocatalytic properties, without needing to perform protein mutation or bioengineering procedures. We demonstrate this strategy using a model heme protein, myoglobin, which is cheap and commercially available, and displays the peroxidase like activity. High purity graphite electrodes were modified with specific π-π stacked nanotube-pyrenyl '3D' nanostructures to accomplish the desired immobilization of myoglobin. We have observed that the type of selective immobilization greatly influences the resulting heterogeneous electron transfer rate constant (k_s in s^{-1}) and electrocatalytic properties (k_{cat}/K_M in M^{-1} s^{-1}) of myoglobin. The favorable orientation of the heme-moiety of protein on the electrode with a minimized electron tunneling barrier for different directed versus random immobilization strategies are investigated. Thus the findings of this study have great potential in guiding the design of novel high performance protein bioreactors and biosensors that may not require the tedious protein amino-acid mutations/engineering to alter catalytic properties.

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