

Electrochemistry of the Blue Copper Protein *Pseudomonas Aeruginosa* Azurin

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The blue copper protein *Pseudomonas aeruginosa* azurin is one of the best-characterized redox metalloproteins. It consists of a single copper centre and 128 amino acid residues, and plays an important role as electron carrier in electron transfer chains. In this work we have investigated comprehensively azurin in the adsorbed state and in homogeneous solution using electrochemistry, XPS, and STM. Azurin can be brought to assemble on gold surfaces in two different orientation modes. As known, the amino acid cystine is also easily self-assembled on Au(111) by S-Au bonds. Azurin molecules are directly linked to Au(111) in a similar way through a disulphide group on the protein surface, with the copper centre facing the solution. XPS, capacitance, and in situ STM data demonstrate clearly the presence of azurin monolayers on Au(111) adsorbed via sulphur. Cyclic voltammetry did not give a detectable signal at the redox potential of azurin, but differential pulse voltammetry exhibits a pair of symmetric redox peaks at 0.116 V vs. SCE indicative that azurin redox function is retained in the adsorbed state. The interfacial electron transfer rate constant could be determined to be 30 s⁻¹ from electrochemical impedance spectroscopy (EIS). In the other adsorption mode azurin is immobilized in a stable monolayer by hydrophobic interactions on variable-length alkanethiols self-assembled on Au(111). In this mode the copper centre is facing the electrode surface. Adsorption and long-range electron tunnelling in this mode have been characterized in detail by electrochemical methods and STM. Azurin voltammetry on graphite electrodes in homogeneous solution is reversible and diffusion controlled. The reduction potential is, interestingly, 10 mV higher in D₂O than in H₂O solution at 298 oK and with a (numerically) significantly higher temperature coefficient (0.87 mV K⁻¹ and 0.59 mV K⁻¹, respectively). This has been assigned to different solvation and thermal expansion of azurin in the two solvents.

References

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