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The Au-S bond in biomolecular adsorption and electrochemical electron transfer

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Interfacial electrochemical electron transfer (ET) of redox metalloproteins is long established[1]. For the proteins to retain full ET or enzyme activity, modification of the electrode surfaces, such as gold surfaces by self-assembled molecular monolayers (SAMs), is nearly always required, where pure and functionalized alkanethiols have emerged as core linkers.

We overview first binding and single-molecule long-range electron transfer of some metalloproteins, metalloenzymes, and DNA-based molecules on single-crystal Au(111), Au(100), and Au(100) electrode surfaces, bound either directly by Au-S linking of surface cysteines to the gold surfaces, or indirectly by non-covalent linking to SAMs of pure and functionalized alkanethiols[1,2]. Core techniques are electrochemistry, surface spectroscopies, and *in situ* STM and AFM under electrochemical potential control, framed by single-molecule charge transport theory and electronic structure computations[3,4]. Molecular packing, voltammetry and *in situ* STM/AFM are found to be exceedingly sensitive to the structure of the thiol-based SAM molecules, testifying both to the crucial importance of the Au-S binding, and to the SAM linking to the protein[2-5].

A primary focus that has emerged is the electronic structure of the Au-S link and the packing of the SAMs[3,4]. We have, first disentangled a wealth of data to identify the nature of the core Au-S contact. All data suggest that the electronic Au-S link is dominated by a Au(0)-thiyl radical with strong van der Waals forces and not by a Au(I)-thiolate ionic/covalent unit. Molecular packing is, further crucially determined by the SAM molecular structure and involves binding either to Au-atoms mined out of the surface or directly to a flat single-crystal surface. We illustrate this by high-resolution *in situ* STM of straight, branched, and chiral alkanethiols on Au(111)-electrode surfaces.

[1] J. Zhang, A.M. Kuznetsov, I.G. Medvedev, Q. Chi, T. Albrecht, P.S. Jensen and J. Ulstrup, *"Single-molecule Electron Transfer in Electrochemical Environments"*, Chem. Rev. 108 (2008) 2737-2791.

[2] P. Salvatore, D. Zeng, K.K. Karlsen, Q. Chi, J. Wengel and J. Ulstrup, *"Electrochemistry of single metalloprotein and DNA-based molecules at Au(111)-electrode surfaces"*, ChemPhysChem 14 (2013) 2101-2111.

[3] J.R. Reimers, M.J. Ford, A. Halder, J. Ulstrup, and N.S. Hush, *"Gold surfaces and nanoparticles are protected by Au(0)-thiyl species and are destroyed when Au(I)-thiolates form"*, Proc. Nat. Acad. Sci. USA 113 (2016) E1424-E1433.

[4] Q. Chi, M.J. Ford, A. Halder, N.S. Hush, J.R. Reimers and J. Ulstrup, *"Sulfur ligand mediated electrochemistry of gold surfaces and nanoparticles: what, how, and why?"*, Curr. Opin. Electrochemistry 1 (2017) 7-15.

[5] N. Zhu, J. Ulstrup and Q. Chi, *"Long-range interfacial electron transfer and electrocatalysis of molecular scale Prussian Blue nanoparticles linked to Au(111)- electrode surfaces by different chemical contacting groups"*, Russ. J. Electrochemistry 53 (2017) in press.