A gold-nanoparticle stoppered [2]rotaxane

The construction of molecular machines has captured the imagination of scientists for decades. Despite significant progress in the synthesis and studies of the properties of small-molecule components (smaller than 2-5 kilo Dalton), challenges regarding the incorporation of molecular components into real devices are still eminent. Nano-sized molecular machines operate the complex biological machinery of life, and the idea of mimicking the amazing functions using artificial nano-structures is intriguing. Both in small-molecule molecular machine components and in many naturally occurring molecular machines, mechanically interlocked molecules and structures are key functional components. In this work, we describe our initial efforts to interface mechanically-interlocked molecules and gold-nanoparticles (AuNPs); the molecular wire connecting the AuNPs is covered in an insulating rotaxane-layer, thus mimicking the macroscopic design of a copper wire. Taking advantage of recent progress in the preparation of supramolecular complexes of the cucurbit[7]uril (CB[7]) macrocycle, we have prepared a bis-thiol functionalised pseudo-rotaxane that enables us to prepare a AuNP-stoppered [2]rotaxane in water. The pseudo-rotaxane is held together extremely tightly (Ka > 10^{13} M^{-1}), Ka being the association constant. We have studied the solution and gas phase guest-host chemistry using NMR spectroscopy, mass spectroscopy, and electrochemistry. The bis-thiol functionalised pseudo-rotaxane holds further a ferrocene unit in the centre of the rotaxane; this ferrocene unit enables us to address the system in detail with and without CB[7] and AuNPs using electrochemical methods.
Chemically controlled interfacial nanoparticle assembly into nanoporous gold films for electrochemical applications

Nanoporous gold (NPG) is an effective material for electrocatalysis and can be made via a dealloy method such as etching of silver–gold alloys. Dealloyed NPG may contain residual silver that affects its catalytic performance. Herein, a different approach has been reported for the formation of NPG at the liquid/air interface starting from gold nanoparticles (AuNPs) in an aqueous solution, providing silver-free gold films. Chloroauric acid is reduced to AuNP building blocks by 2-(N-morpholino)ethanesulfonic acid, which also acts as a protecting agent and pH buffer. By adding potassium chloride before AuNP synthesis and hydrochloric acid to the resultant AuNP solutions, we can reproducibly obtain continuous gold networks. The sintered AuNPs produced by this method result in chemically synthesized nanoporous gold films (cNPGFs) that resemble dealloyed NPG in terms of morphology and porosity; additionally, they can be controlled by varying the temperature, chloride concentration, ionic strength, and protonation of the buffer. cNPGF formation is attributed to the destabilization of AuNPs at the air–liquid interface. The developed method generates electrochemically stable cNPGFs up to 20 cm² in size with an average thickness of 500 ± 200 nm, areal density of 50–150 μg cm⁻², and porosity as high as 85%. Importantly, cNPGFs can effectively catalyze both CO₂ reduction and CO oxidation electrochemically. Thus, the developed synthetic method offers large-scale production of pure bottom-up NPGFs for multifarious electrocatalytic applications.

General information
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Organisations: Department of Energy Conversion and Storage, Department of Chemistry, NanoChemistry, Organic Chemistry, Department of Biotechnology and Biomedicine, Technical University of Denmark
Authors: Christiansen, M. U. -. (Ekstern), Seselj, N. (Intern), Engelbrekt, C. (Intern), Wagner, M. (Intern), Stappen, F. N. (Ekstern), Zhang, J. (Intern)
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Electrochemistry of single molecules and biomolecules, molecular scale nanostructures, and low-dimensional systems

Electrochemistry at ultra-small scales, where even the single molecule or biomolecule can be characterized and manipulated, is on the way to a consolidated status. At the same time molecular electrochemistry is expanding into other areas of sophisticated nano- and molecular scale systems including molecular scale metal and semiconductor nanoparticles (NPs) and other nanostructures, e.g. nanotubes, “nanoflowers” etc.. The new structures offer both new electronic properties and highly confined novel charge transfer environments.

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Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, Kazan National Research Technological University
Authors: Nazmutdinov, R. R. (Ekstern), Zinkicheva, T. T. (Ekstern), Zinkicheva, T. T. (Ekstern), Shermukhamedov, S. A. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
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General Syntheses of Nanotubes Induced by Block Copolymer Self-Assembly

Amphiphilic block copolymer templating strategies are extensively used for syntheses of mesoporous materials. However, monodisperse tubular nanostructures are limited. Here, a general method is developed to synthesize monodisperse nanotubes with narrow diameter distribution induced by self-assembly of block copolymer. 3-Aminophenol (AP) and formaldehyde (F) polymerize and self-assemble with cylindrical PS-b-PEO micelles into worm-like PS-b-PEO@APF composites with uniform diameter (49 ± 3 nm). After template extraction, worm-like APF polymer nanotubes are formed. The structure and morphology of the polymer nanotubes can be tuned by regulating the synthesis conditions. Furthermore, PS-b-PEO@APF composites are uniformly converted to isomorphic carbon nanotubes with large surface area of 662 m² g⁻¹, abundant hierarchical porous frameworks and nitrogen doping. The synthesis can be extended to silica nanotubes. These findings open an avenue to the design of porous materials with controlled structural framework, composition, and properties for a wide range of applications.
Redox Potentials and Electronic States of Iron Porphyrin IX Adsorbed on Single Crystal Gold Electrode Surfaces

Metalloporphyrins are active sites in metalloproteins and synthetic catalysts. They have also been studied extensively by electrochemistry as well as being prominent targets in electrochemical scanning tunneling microscopy (STM). Previous studies of FePPIX adsorbed on graphite and alkylthiol modified Au electrodes showed a pair of reversible Fe(III/II)PPIX peaks at about -0.41 V (vs NHE) at high solution pH. We recently used iron protoporphyrin IX (FePPIX) as an intercalating probe for long-range electrochemical electron transfer through a G-quadruplex oligonucleotide (DNAzyme); this study disclosed two, rather than a single pair of voltammetric peaks with a new and dominating peak, shifted 200 mV positive relative to the approximate to-0.4 V peak. Prompted by this unexpected observation, we report here a study of the voltammetry of FePPIX itself on single-crystal Au(111), (100), and (110) and polycrystalline Au electrode surfaces. In all cases the dominating pair of new Fe(III/II)PPIX redox peaks, shifted positively by more than 200 mV compared to those of previous studies appeared. This observation is supported by density functional theory (DFT) which shows that strong dispersion forces in the FePPIX/Au electronic interaction drive the midpoint potential toward positive values. The FePPIX spin states depend on interaction with the Au(111) interface, converting all the Fe(II)/(III)PPIX species into low-spin states. These results support electrochemical evidence for the nature of the electronic coupling between FePPIX and Au-surfaces, and the electronic states of adsorbate molecules, with a bearing also on recent reports of magnetic FePPIX/Au(111) interactions in ultrahigh vacuum (UHV).

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Authors: Zhang, L. (Intern), Kepp, K. P. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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Tailored Electron Transfer Pathways in Aucore/Ptshell-Graphene Nanocatalysts for Fuel Cells

Aucore/Ptshell-graphene catalysts (G-Cys-Au@Pt) are prepared through chemical and surface chemical reactions. Au–Pt core–shell nanoparticles (Au@Pt NPs) covalently immobilized on graphene (G) are efficient electrocatalysts in low-temperature polymer electrolyte membrane fuel cells. The 9.5 ± 2 nm Au@Pt NPs with atomically thin Pt shells are attached on graphene via L-cysteine (Cys), which serves as linkers controlling NP loading and dispersion, enhancing the Au@Pt NP stability, and facilitating interfacial electron transfer. The increased activity of G-Cys-Au@Pt, compared to non-chemically immobilized G-Au@Pt and commercial platinum NPs catalyst (C-Pt), is a result of (1) the tailored electron transfer pathways of covalent bonds integrating Au@Pt NPs into the graphene framework, and (2) synergetic electronic effects of atomically thin Pt shells on Au cores. Enhanced electrocatalytic oxidation of formic acid, methanol, and ethanol is observed as higher specific currents and increased stability of G-Cys-Au@Pt compared to G-Au@Pt and C–Pt. Oxygen reduction on G-Cys-Au@Pt occurs at 25 mV lower potential and 43 A gPt−1 higher current (at 0.9 V vs reversible hydrogen electrode) than for C–Pt. Functional tests in direct formic acid, methanol and ethanol fuel cells exhibit 95%, 53%, and 107% increased power densities for G-Cys-Au@Pt over C–Pt, respectively.

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Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, Tianjin University, Danish Power Systems Ltd.
Authors: Seselj, N. (Intern), Engelbrekt, C. (Intern), Ding, Y. (Ekstern), Hjuler, H. A. (Ekstern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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Scopus rating (2014): SJR 6.706 SNIP 2.975 CiteScore 15.27
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Three-dimensional iron sulfide-carbon interlocked graphene composites for high-performance sodium-ion storage

Three-dimensional (3D) carbon-wrapped iron sulfide interlocked graphene (Fe7S8@C-G) composites for high-performance sodium-ion storage are designed and produced through electrostatic interactions and subsequent sulfurization. The iron-based metal–organic frameworks (MOFs, MIL-88-Fe) interact with graphene oxide sheets to form
3D networks, and carbon-wrapped iron sulfide (Fe$_7$S$_8$@C) nanoparticles with high individual-particle conductivity are prepared following a sulfurization process, surrounded by interlocked graphene sheets to enhance the interparticle conductivity. The prepared Fe$_7$S$_8$@C-G composites exhibit not only improved individual-particle and interparticle conductivity to shorten electron/ion diffusion pathways, but also enhanced structural stability to prevent the aggregation of active materials and buffer large volume changes during sodiation/desodiation. As a sodium-ion storage material, the Fe$_7$S$_8$@C-G composites exhibit a reversible capacity of 449 mA h g$^{-1}$ at 500 mA g$^{-1}$ after 150 cycles and a retention capacity of 306 mA h g$^{-1}$ under a current density of 2000 mA g$^{-1}$. The crucial factors related to the structural changes and stability during cycles have been further investigated. These results demonstrate that the high-performance sodium-ion storage properties are mainly attributed to the uniquely designed three-dimensional configuration.

**General information**

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Organisations: Department of Chemistry, NanoChemistry, Department of Micro- and Nanotechnology, Molecular Windows, Organic Chemistry, Shandong University, University of Limerick
Authors: Huang, W. (Intern), Sun, H. (Intern), Shangguan, H. (Ekstern), Cao, X. (Intern), Xiao, X. (Ekstern), Shen, F. (Intern), Mølhave, K. (Intern), Ci, L. (Ekstern), Si, P. (Ekstern), Zhang, J. (Intern)
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**A straight forward approach to electrodeposit tungsten disulfide/poly(3,4-ethylenedioxythiophene) composites onto nanoporous gold for the hydrogen evolution reaction**
1.1nm tungsten disulfide/poly(3,4-ethylenedioxythiophene) (PEDOT) was successfully electrodeposited on the surface of dealloyed nanoporous gold (NPG) surface to form uniform nanocomposites and offers an excellent electrocatalysis for the electrochemical dihydrogen evolution reaction (HER) in acidic media. The approach is straight forward and does not require any expensive equipment or intensive energy. The morphology and composition of the nanocomposites were structurally mapped by high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrometry (FTIR). The roles of both the NPG substrate and PEDOT in the observed enhanced HER activity compared to planar Au-electrode surfaces and pure single-component WS₂ have been deconvoluted experimentally. PEDOT itself is inert for the HER, but was found to improve significantly the conductivity and operating stability of the WS₂ catalyst. The prepared nanocomposites reach the best in 2D WS₂ catalyst family, exhibiting excellent electrochemical catalytic activity for the HER. The optimal electrode showed an onset potential of -164 mV vs. reversible hydrogen electrode (RHE), an apparent exchange current density as high as 0.04 mAcm⁻², and a very low Tafel slope of 53mV dec⁻¹. These catalysts are promising electrocatalysts for generation a large amount of H₂ from water.

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Authors: Xiao, X. (Ekstern), Engelbrekt, C. (Intern), Zhang, M. (Intern), Li, Z. (Ekstern), Ulstrup, J. (Intern), Zhang, J. (Intern), Si, P. (Ekstern)
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Web of Science (2014): Indexed yes
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Scopus rating (2013): SJR 0.965 SNIP 1.488 CiteScore 2.78
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Scopus rating (2012): SJR 0.918 SNIP 1.373 CiteScore 2.26
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Scopus rating (2011): SJR 0.908 SNIP 1.402 CiteScore 2.27
ISI indexed (2011): ISI indexed yes
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BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.924 SNIP 1.141
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Scopus rating (2009): SJR 0.842 SNIP 1.023
Web of Science (2009): Indexed yes
Bacterial Electrocatalysis of K₄[Fe(CN)₆] Oxidation

*Shewanella oneidensis* MR-1 (MR-1), a model strain of electrochemically active bacteria, can transfer electrons from cell to extracellular electron acceptors including Fe(III) (hydro)oxides. It has been reported that several redox species such as cytochromes in membranes and flavins assist in the electron transport (ET) processes. However, the oxidization of metal compounds was barely described. Here we report electrocatalysis of K₄[Fe(CN)₆] oxidation by MR-1. K₄[Fe(CN)₆] is a redox inorganic compound and shows a reversible redox process on bare glassy carbon (GCE). This is reflected by a pair of symmetric peaks on cyclic voltammetry (CV) (Fig. 1). Interestingly, unsymmetric peaks with a strong anodic peak and a very weak cathodic peak are found on CVs of 1.0 mM K₄[Fe(CN)₆] when the GCE was coated with MR-1, distinguished from the reversible CV on bare electrodes (Fig. 1). A similar electrochemical pattern has been observed using K₃[Fe(CN)₆]. These results suggested an electrocatalysis process of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻ by MR-1. The ratio of anodic peak current vs cathodic peak current depends on scan rate, suggesting both diffusion of redox molecules and interfacial ET rate are key factors of the electrocatalysis. Moreover, Selectivity of MR-1 is another interesting issue: MR-1 does not catalyze other redox compounds such as Ru[(NH₃)₆]Cl₃ and Resorufin. In our recent work, extracellular polymeric substances (EPS) showed redox properties and electron hopping through EPS. Here we notice that neither the glassy carbon electrode (GCE) coating EPS extracted from MR-1 nor MR-1 removed EPS (MR-1ΔEPS) exhibited asymmetric redox feature (Fig.1), but caused the decrease of current and the broadening of the difference of anodic and cathodic peak potential, indicating the hindrance of reaction. More work to disclose the origin of the electrocatalysis phenomenon is in progress, aiming at the identification of related compositions in MR-1.

Bacterial Electrocatalysis of K₄[Fe(CN)₆] Oxidation

*Shewanella oneidensis* MR-1 (MR-1), a model strain of electrochemically active bacteria, can transfer electrons from cell to extracellular electron acceptors including Fe(III) (hydro)oxides. It has been reported that several redox species such as cytochromes in membranes and flavins assist in the electron transport (ET) processes. However, the oxidization of metal compounds was barely described. Here we report electrocatalysis of K₄[Fe(CN)₆] oxidation by MR-1. K₄[Fe(CN)₆] is a redox inorganic compound and shows a reversible redox process on bare glassy carbon (GCE). This is reflected by a pair of symmetric peaks on cyclic voltammetry (CV) (Fig. 1). Interestingly, unsymmetric peaks with a strong anodic peak and a very weak cathodic peak are found on CVs of 1.0 mM K₄[Fe(CN)₆] when the GCE was coated with MR-1, distinguished from the reversible CV on bare electrodes (Fig. 1). A similar electrochemical pattern has been observed using K₃[Fe(CN)₆]. These results suggested an electrocatalysis process of [Fe(CN)₆]⁴⁻ to [Fe(CN)₆]³⁻ by MR-1. The ratio of anodic peak current vs cathodic peak current depends on scan rate, suggesting both diffusion of redox molecules and interfacial ET rate are key factors of the electrocatalysis. Moreover, Selectivity of MR-1 is another interesting issue: MR-1 does not catalyze other redox compounds such as Ru[(NH₃)₆]Cl₃ and Resorufin. In our recent work, extracellular polymeric substances (EPS) showed redox properties and electron hopping through EPS. Here we notice that neither the glassy carbon electrode (GCE) coating EPS extracted from MR-1 nor MR-1 removed EPS (MR-1ΔEPS) exhibited asymmetric redox feature (Fig.1), but caused the decrease of current and the broadening of the difference of anodic and cathodic peak potential, indicating the hindrance of reaction. More work to disclose the origin of the electrocatalysis phenomenon is in progress, aiming at the identification of related compositions in MR-1.

**General information**

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**Organisations:** Department of Chemistry, NanoChemistry, Metalloprotein Chemistry and Engineering, Organic Chemistry, Chinese Academy of Sciences

**Authors:** Zheng, Z. (Intern), Xiao, Y. (Intern), Wu, R. (Intern), Christensen, H. E. M. (Intern), Zhao, F. (Ekstern), Zhang, J. (Intern)

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Chemical Synthesis and Electrochemical Characterization of Nanoporous Gold films

Nanoporous gold (NPG) is conventionally made via dealloying methods. We present an alternative method for bottom-up chemical synthesis of nanoporous gold film (cNPGF), with properties resembling those of dealloyed NPG. The developed procedure is simple and only benign chemicals are used. Chloroauric acid is reduced to nanoparticles (NPs) by 2-(N-morpholino)ethanesulfonate, acting also as a protecting agent for the NPs and as a pH buffer, while potassium chloride is used to control ionic strength. The film formation is controlled by parameters such as temperature, ionic strength and protonation of the buffer. Therefore, it is possible to influence the trapping of nanoparticles at the air-liquid interface, yielding porous thin film structures, Figure 1A. The produced cNPGFs have been investigated by atomic force microscopy (AFM), transmission electron microscopy (TEM) and cyclic voltammetry (CV). The micro- and nanostructure of cNPGFs are shown in Figure 1B and 1C. The film coverage areas that we can achieve are up to 20 cm², with an average thickness of 500 ± 200 nm. It is also found that in-house synthesized cNPGFs are active electrocatalysts for CO₂ reduction and CO oxidation.

Electrocatalysis of Gold Nanostructures for Electrochemical Energy Conversion

Electrocatalytic oxidation of K₄[Fe(CN)₆] by metal-reducing bacterium Shewanella oneidensis MR-1

The microbial metabolic activities between metals and bacteria play a vital role on biogeochemical cycling of metal compounds. One of these activities is extracellular electron transfer (EET), in which some microbes exchange electrons with external redox minerals, electrodes, or even other microorganisms. The bacteria can either take electrons or give electrons. Shewanella oneidensis MR-1 (MR-1) is electrochemical active, it can transfer electrons from cell to extracellular electron acceptors including Fe(III) (hydro)oxides. In this study, we report that MR-1 electrocatalyze the oxidation of an inorganic redox compound K₄[Fe(CN)₆]⁴⁻. A pair of symmetric peak in the cyclic voltammetry (CV) of K₄[Fe(CN)₆] were found on bare glassy carbon electrode (GCE). Surprisingly, when the GCE is coated MR-1, the anodic peak almost sustained at the same level; while the cathodic peak apparently shrunk. We attribute this phenomenon to the electrocatalytic oxidation by MR-1. The discovery of the ability to oxidize [Fe(CN)₆]⁴⁻ by MR-1 broadens our horizon of the role that dissimilatory metal reduction bacteria play in the environment.
Electrochemical Catalysis of Inorganic Complex $\text{K}_4[^{39}\text{Fe(CN)}_6]$ by Shewanella oneidensis MR-1

The interaction between metal and bacteria is a universal and important biogeochemical process in the environment. As a dissimilatory metal reduction bacterium, the electrochemically active bacterium Shewanella oneidensis MR-1 can transfer intracellular electrons to minerals. This ability is attributed to the redox proteins localized on the outer membrane, for example, the MtrC, MtrB, MtrA and CymA. Here we investigate its electrochemical properties towards redox compounds. It shows strong electrocatalysis toward electrochemical oxidation of $\text{K}_4[^{39}\text{Fe(CN)}_6]$. As a redox molecule, $\text{K}_4[^{39}\text{Fe(CN)}_6]$ gives a pair of redox peaks on voltammetry on bare glassy carbon electrode (GCE), symmetric with ideal peak-peak separation of about 60 mV, indicating a reversible one-electron transfer process (blue curve, Figure 1). Surprisingly, the presence of S. oneidensis MR-1 on GCE results in an asymmetric redox peak, with almost disappearance of the cathodic peak and strengthening of the anodic peak, which is a typical catalysis feature of electrochemical oxidation. Further experiments show that S. oneidensis MR-1 does not give such electrocatalysis to redox compounds such as Ru[(NH$_3$)$_6$]Cl$_3$ and Resorufin. Selectivity and electrocatalysis mechanisms of S. oneidensis MR-1 are under investigation. The ability of S. oneidensis MR-1 to catalyze redox action of inorganic metal complex compounds will provide an insight on metal cycles in nature.

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Electrochemical single-molecule conductivity of duplex and quadruplex DNA

Photoinduced and electrochemical charge transport in DNA (oligonucleotides, OGNs) and the notions “hopping”, superexchange, polaron, and vibrationally gated charge transport have been in focus over more than two decades. In recent years mapping of electrochemical charge transport of pure and redox marked single- and double-strand OGNs has reached the single-molecule level based i.a. on electrochemical in situ scanning tunnelling microscopy (STM) and break-junction (B-J) STM. There are much fewer such reports on “non-canonical” OGN structures such as G-quadruplexes. We discuss first single-molecule electrochemical conductivity of pure and redox marked duplex OGNs, and address next electrochemistry and electrochemical conductivity in the few reported monolayer and single-molecule G-quadruplex studies. Facile electrochemical electron transfer of iron protoporphyrin IX stacked onto three-quartet 12-guanine quadruplex (“DNAzyme”) and in situ high-resolution molecular structures are particularly noted.

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Extracellular polymeric substances act as transient media in extracellular electron transfer of Shewanella oneidensis MR-1

It is well known that microorganism is surrounded by extracellular polymeric substances (EPS) which include polysaccharides, proteins, glycoproteins, nucleic acids, phospholipids, and humic acids. However, previous studies on microbial extracellular electron transfer (EET) are conducted on cells without extracting EPS or cells collected from log stage or early-steady stage cultures with little EPS. Therefore, microbial cells are believed in contact directly with each other or electrode. Such attempt apparently ignored the role of EPS in microbial EET, even though many components of EPS, such as DNA, humic acids and some proteins, are electrochemically active or semiconductive. Herein, we report experimental evidences of EPS role on EET for Shewanella oneidensis MR-1. Atomic force microscopy clearly showed that the cell surface was cleaned and few EPS could be observed on MR-1 after the extraction. Comparing to cells in control group, MR-1 treated at 38 °C for EPS extraction showed different electrochemical characterizations as revealed by differential pulse voltammetry. EPS extracted from MR-1 also was proved to be electrochemically active. The present study indicated that EPS play important roles in EET of MR-1.

Extracellular polymeric substances are transient media for microbial extracellular electron transfer

Microorganisms exploit extracellular electron transfer (EET) in growth and information exchange with external environments or with other cells. Every microbial cell is surrounded by extracellular polymeric substances (EPS). Understanding the roles of three-dimensional (3D) EPS in EET is essential in microbiology and microbial exploitation for mineral bio-respiration, pollutant conversion, and bioenergy production. We have addressed these challenges by comparing pure and EPS-depleted samples of three representative electrochemically active strains viz Gram-negative Shewanella oneidensis MR-1, Gram-positive Bacillus sp. WS-XY1, and yeast Pichia stipites using technology from electrochemistry, spectroscopy, atomic force microscopy, and microbiology. Voltammetry discloses redox signals from cytochromes and flavins in intact MR-1 cells, whereas stronger signals from cytochromes and additional signals from both flavins and cytochromes are found after EPS depletion. Flow cytometry and fluorescence microscopy substantiated by N-acetylglucosamine and electron transport system activity data showed less than 1.5% cell damage after EPS extraction. The electrochemical differences between normal and EPS-depleted cells therefore originate from electrochemical species in cell walls and EPS. The 35 ± 15-nm MR-1 EPS layer is also electrochemically active itself, with cytochrome electron transfer rate constants of 0.026 and 0.056 s⁻¹ for intact MR-1 and EPS-depleted cells, respectively. This surprisingly small rate difference suggests that molecular redox species at the core of EPS assist EET. The combination of all the data with electron transfer analysis suggests that electron "hopping" is the most likely molecular mechanism for electrochemical electron transfer through EPS.
Graphene-glucose oxidase bioanodes for enzymatic biofuel cells

Enzymatic biofuel cells (EBFCs) are electrochemical devices, that produce electricity from energy stored in fuel molecules under catalysis of enzymes. An EBFC contains a bioanode and/or a biocathode, in which enzymes are used to catalyse oxidation of fuel molecules such as sugars, and dioxygen reduction, respectively. The advantage of EBFCs is to generate energy from abundant fuel molecules without using expensive noble metals. On the other hand, development of EBFCs is still at the research stage due to instability of the biocatalysts. Here, we are developing a bioanode using graphene as supporting material, polyethyleneimine (PEI) as linker and glucose oxidase (GOD) as the chosen enzyme. GOD can catalyze oxidation of glucose to gluconolactone, but needs a mediator to assist electron transfer between the enzyme and electrodes. The redox molecule ferrocene carboxylic acid (FcCOOH) is immobilized together with GOD on the bioanode. Structure and composition of the graphene-GOD bioanode are shown in Fig. 1b. Electrochemical catalytic performance of the prepared bioanode has been observed. An EBFCs with the bioanode and the commercial Pt cathode have been successfully assembled and systematically investigated. The assembled EBFCs show good reproducibility. EBFCs provide maximum output power density 2.47 μW cm⁻² at 35 ℃, indicating the optimized activity of EBFCs fed with glucose.

Ligations of Gold Atoms with Iron Porphyrin

Gold is an exotic material with d-electrons deciding electronic mappings and configurations of adsorbed molecules. The specific interaction of Au atoms and S-, Ncapped molecules make gold nanoparticles widely applied in the medicine transport and immunoassay. Density functional theory demonstrates that the electronic structure of Au adatoms is d⁹s¹ but not d¹⁰s⁰ in the forms of Au-thiolates. The surrounding Au surface atoms are passivated leading to both Au-Au and S-S interactions. A wide range of surface phenomena of nanoparticle size-control and break-junctions in surface physics and chemistry including electrochemistry and electrochemical scanning tunneling microscopy (in situ STM) are explained with this theory. Iron porphyrin is a well-known active redox center of cytochrome c and hemoglobin/myoglobin assisting membrane-crossing electron transfer or blood oxygen transport. The electronic states and configurations of iron porphyrin affect the electrochemical properties of the metalloproteins, where the artificial constructed proteins are designed by the mutations of amino residues or the structural optimizations of iron porphyrins. Iron porphyrin adsorption on graphite and graphene surfaces by π-π electron stacking has been widely studied and the catalytic activity found to be enhanced warranting the notion of enzyme mimics. Weak physisorption was, however, recently observed by in situ STM, but the electronic properties of iron porphyrin adsorbed on gold has not been addressed before. This issue is, however, critical. We report here a study of ironporphyrin on the three low-index Au-surfaces using a combination of electrochemistry and density functional theory.
Metal-Organic Framework Derived FeP/C Interlocked Graphene Hybrid Composite for Hydrogen Evolution Reaction

Microwave synthesis of metal nanocatalysts for the electrochemical oxidation of small biomolecules

Electrochemical oxidation of small biomolecules provides an approach to generate clean energy from a sustainable resource. It serves as a principle for anode reactions in fuel cells to convert energy stored in chemical bonds into electrical power. Efficient and robust nanocatalysts are essential to reduce the reaction barrier and accelerate the reaction kinetics. First the general aspects of electrochemical oxidation of small biomolecules are outlined and the green synthesis of metal particles by microwave synthesis is compared to conventional heating synthesis. Then recent progress in microwave-assisted nanocrystals used for electrochemical oxidation of small biomolecules is reviewed for alcohols, acids, and glucose. The challenges and future perspectives for the microwave synthesis as well as electrochemical oxidation of small biomolecules are discussed.
Nanoengineering of graphene supported functional composites for performance enhanced enzymatic biofuel cells

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry
Authors: Shen, F. (Intern), Cao, X. (Intern), Pankratov, D. (Intern), Zhang, J. (Intern), Chi, Q. (Intern)
Pages: 219-240
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Nanoscale engineering of 3D graphene foams for enzyme immobilization and enhanced bioelectrocatalysis

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, Novozymes A/S
Authors: Shen, F. (Intern), Zhang, J. (Intern), Ulstrup, J. (Intern), Østergaard, L. H. (Ekstern), Chi, Q. (Intern)
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Publication date: 2017

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Main Research Area: Technical/natural sciences
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Plasmon-enhanced Solar Fuel Production with Gold-metal Oxide Hybrid Nanomaterials
Harnessing sunlight to drive chemical reactions for energy storage is an important element in the transition towards green and sustainable technologies. Solar fuel production using semiconductor nanoparticles (SNPs) are widely studied but suffer from poor utilization of the solar spectrum and/or poor stability under operating conditions. A new avenue addressing these challenges involve plasmonic metal nanoparticles (PNPs). These stable materials have tunable optical properties and exciting catalytic behavior. Composite photocatalysts of SNPs and PNPs exploit the majority of the solar spectrum, provide new catalytic routes and expands the scope of solar photocatalysis. We prepare metal oxide SNPs, gold PNPs and their hybrids through mild aqueous syntheses to develop efficient photocatalyst for solar fuel production. Focus is placed on the synergetic interplay between SNPs and PNPs, understanding the complex pathways, and disentangling plasmon-driven, photothermal and heterogenous catalytic effects.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, University of California
Authors: Engelbrekt, C. (Intern), Law, M. (Ekstern), Zhang, J. (Intern)
Publication date: 2017
Event: Poster session presented at TMS 2017, San Diego, United States.
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Electronic versions:
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Roles of extracellular polymeric substances in microbial extracellular electron transfer

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, Chinese Academy of Sciences
Authors: Xiao, Y. (Intern), Ulstrup, J. (Intern), Zhao, F. (Ekstern), Zhang, J. (Intern)
Number of pages: 1
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Publication: Research - peer-review › Conference abstract in proceedings – Annual report year: 2017

Side Effect of Good's Buffers on Optical Properties of Gold Nanoparticle Solutions
In the search of fluorescent nanoclusters for bioimaging, several synthetic methods have been attempted. Particularly, the formation of gold nanoclusters during synthesis of gold nanoparticles (AuNPs) using Good’s buffers has been achieved. Here 2-(N-morpholino)ethanesulfonic acid (MES), 3-(N-morpholino)propanesulfonic acid (MOPS) and 4-(N-morpholino)butanesulfonic acid (MOBS) are chosen Good’s buffers. Resultant AuNP solutions have been subjected to electrochemical investigations along with UV-vis and fluorescent spectroscopies. Distinct absorption features at ca. 290 and 360 nm and fluorescence emission in range of 350-485 nm are observed in filtrated AuNP-free solutions. Notably, electrochemical oxidation of the buffers generates similar optical properties, suggesting that the degradation products of these compounds contribute significantly to the optical properties in AuNP solutions. This work indicates a need for deeper evaluation of fluorescence signals based on metal nanoparticles or nanoclusters.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, Metalloprotein Chemistry and Engineering, Technical University of Denmark, East China University of Science and Technology
Authors: Wagner, M. (Intern), Engelbrekt, C. (Intern), Undall-Behrend Christiansen, M. (Ekstern), Christensen, H. E. M. (Intern), Qian, X. (Ekstern), Ulstrup, J. (Intern), Zhao, C. (Ekstern), Zhang, J. (Intern)
Publication date: 2017
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Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2017

Simultaneous modulation of surface composition, oxygen vacancies and assembly in hierarchical Co₃O₄ mesoporous nanostructures for lithium storage and electrocatalytic oxygen evolution
We developed a facile solution reductive method to simultaneously tune the surface composition, oxygen vacancies and three dimensional assembly in Co₃O₄ hierarchical nanostructures. The controllable surface composition, oxygen vacancies together with hierarchical micro/nanarchitectures resulted in superior electrochemical properties when used as the anode materials for lithium-ion batteries and as an electrocatalyst for the oxygen evolution reaction. The excellent electrochemical performance is attributed to the synergistic effects of novel hierarchical morphology, crystal structure of the active materials, the improvement of intrinsic conductivity and inner surface area induced by the oxygen vacancies. The present strategy not only provides a facile method to assemble novel hierarchical architectures, but also paves a way to control surface structures (chemical composition and crystal defects) in other transition-metal compounds, and thus will hold great promise in the fields of energy storage and conversion.

General information
State: Published
Organisations: Department of Micro- and Nanotechnology, Molecular Windows, Department of Chemistry, NanoChemistry, Organic Chemistry, Boston College
Authors: Sun, H. (Intern), Zhao, Y. (Ekstern), Mølhave, K. (Intern), Zhang, M. (Intern), Zhang, J. (Intern)
Pages: 14431-14441
The Au-S bond in biomolecular adsorption and electrochemical electron transfer

Interfacial electrochemical electron transfer (ET) of redox metalloproteins is long established. 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. 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. 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. A primary focus that has emerged is the electronic structure of the Au-S link and the packing of the SAMs. 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 vander 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.
The Pathogenic A2V Mutant Exhibits Distinct Aggregation Kinetics, Metal Site Structure, and Metal Exchange of the Cu$^{2+}$-Aβ Complex

A prominent current hypothesis is that impaired metal ion homeostasis may contribute to Alzheimer's disease (AD). We elucidate the interaction of Cu$^{2+}$ with wild-type (WT) Aβ$_{1-40}$ and the genetic variants A2T and A2V which display increasing pathogenicity as A2T<WT<A2V. Cu$^{2+}$ significantly extends the lag phase in aggregation kinetics, in particular for the pathogenic A2V variant. Additionally, a rapid, initial, low intensity ThT response is observed, possibly reflecting formation of Cu$^{2+}$ induced amorphous aggregates, as supported by atomic force microscopy (AFM) and circular dichroism (CD) spectroscopy, again most notably for the A2V variant. Electron paramagnetic resonance (EPR) spectroscopy gives p $K_a$ values for transition between two Cu$^{2+}$ coordination geometries (component I and II) of 7.4 (A2T), 7.9 (WT), and 8.4 (A2V), that is, component I is stabilized at physiological pH in the order A2T<WT<A2V. $^1$H NMR relaxation exhibits the same trend for the non-coordinating aromatic residues (A2T<WT<A2V), and implies markedly faster inter-peptide Cu$^{2+}$ exchange for the A2V variant than for WT and A2T. We therefore hypothesize that component I of the Cu–Aβ complex is related to pathogenicity, accounting for both the pathogenic nature of the A2V variant and the protective nature of the A2T variant.
Unexpected interactions between gold and N-morpholino-sulfonates

Nanoporous gold (NPG) has a high surface area and excellent conductivity. It is an ideal supporting material for the electrocatalysis, e.g., in fuel cell applications. NPG is traditionally produced by etching a gold/silver alloy. This method has significant drawbacks, such as the introduction of silver into your NPG, and its multi-step fabrication. A method has been discovered for producing NPG as a thin film chemically. This bottom-up approach entails reduction of Au$^{3+}$ precursor using morpholinoethanesulfonic acid (MES). This produces a thin and highly porous gold film at the air-Water interface \(^1\) (for details, see poster by Mikkel Christiansen). This chemical reaction is far more complex than first expected and bi-products, intermediates and reaction mechanisms are the focus of the present work. The chemical reaction and its products have been examined using state-of-the-art nuclear magnetic resonance (NMR), ultraviolet-visible spectroscopy (UV-vis), fluorescence spectroscopy, density functional theory (DFT), mass spectrometry (MS) and Raman spectroscopy. The results illustrate a complex chain of reactions resulting in gold nanoparticles, NPG, and several previously unidentified Au-complexes. \textit{N}-NMR presented three different $^{13}\text{C}$ environments for the N-atom in MES, while the UV-vis results points towards some interesting gold complexes. MS identifies several distinct molecular entities demonstrating the reactivity of...
MES and Au, and fluorescence spectroscopy suggests the formation of polynuclear Au complexes as previously reported where Au nuclei are bridged by C=N functionalities in small organic molecules \(^2\). This adds up to a complicated reaction mechanism involving some interesting Au \(^{3+}/^{1+}\) complexes, deprotonation and oxidation of MES and the formation of molecules that show UV-vis absorbance and fluorescent.

**General information**

**State:** Published

**Organisations:** Department of Chemistry, NanoChemistry, Organic Chemistry, University of California, San Diego, University of Copenhagen

**Authors:** Nielsen, F. S. (Intern), Engelbrekt, C. (Intern), Elliot, S. G. (Intern), Junor, G. (Ekstern), Sørensen, K. (Ekstern), Jensen, K. J. (Ekstern), Clausen, M. H. (Intern), Zhang, J. (Intern)

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**Main Research Area:** Technical/natural sciences

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**Atomically thin Pt shells on Au nanoparticle cores: facile synthesis and efficient synergetic catalysis**

We present a facile synthesis protocol for atomically thin platinum (Pt) shells on top of gold (Au) nanoparticles (NPs) (Au@PtNPs) in one pot under mild conditions. The Au@PtNPs exhibited remarkable stability (> 2 years) at room temperature. The synthesis, bimetallic nanostructures and catalytic properties were thoroughly characterized by ultraviolet-visible light spectrophotometry, transmission electron microscopy, nanoparticle tracking analysis and electrochemistry. The 8 ± 2 nm Au@PtNPs contained 24 ± 1 mol% Pt and 76 ± 1 mol% Au corresponding to an atomically thin Pt shell. Electrochemical data clearly show that the active surface is dominated by Pt with a specific surface area above 45 m² per gram of Pt. Interactions with the Au core increase the activity of the Pt shell by up to 55% and improve catalytic selectivity compared to pure Pt. The Au@Pt NPs show exciting catalytic activity in electrooxidation of sustainable fuels (i.e. formic acid, methanol and ethanol), and selective hydrogenation of benzene derivatives. Especially high activity was achieved for formic acid oxidation, 549 mA (mgPt)⁻¹ (at 0.6 V vs. SCE), which is 3.5 fold higher than a commercial < 5 nm PtnP catalyst. Excellent activity for the direct production of y-valerolactone, an alternative biofuel/fuel additive, from levulinic acid and methyl levulinate was finally demonstrated.

**General information**

**State:** Published

**Organisations:** Department of Chemistry, NanoChemistry, Organic Chemistry, Centre for Catalysis and Sustainable Chemistry

**Authors:** Engelbrekt, C. (Intern), Seselj, N. (Intern), Poreddy, R. (Intern), Riisager, A. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)

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BFI (2015): BFI-level 1

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BFI (2014): BFI-level 1
We have studied electron transfer between cytochrome c and the chiral transition-metal complex pair Λ- and Δ-[Co(Ox)_3]^{3-} (Ox^{2-} = oxalate) via strong ion-pair formation. Chirality was found in both ion-pair formation and electron transfer, with the Λ enantiomer the more strongly bound and faster reacting. Investigations of the chirality using electron-transfer theory combined with quantum-chemical and statistical-mechanical calculations showed that chirality is solely in inter-reactant interaction and electronic overlap.
Harnessing sunlight and storing the energy in chemical bonds is an important element in the transition towards green and sustainable technologies. Solar fuel production requires photocatalysts that (1) absorb large parts of the solar spectrum, (2) generate charges with significant lifetimes and appropriate energies, (3) catalyze relevant chemical transformations from abundant, low-energy starting materials, and (4) are stable under operating conditions. A new avenue within solar fuels involve plasmonic metal nanoparticles (PNPs). These materials have tunable optical properties, exciting catalytic behavior, and can be more stable under operating conditions. Composite photocatalysts of semiconductor nanoparticles (SNPs) and PNPs exploit broadly the solar spectrum, provide new catalytic routes and expand the scope of solar photocatalysis. The newly initiated project aims at developing composite nanomaterials of SNPs and PNPs from mild, aqueous synthesis protocols and testing the catalytic properties of these plasmonic photocatalysts.
Construction of Insulin 18-mer Nanoassemblies Driven by Coordination to Iron(II) and Zinc(II) Ions at Distinct Sites

Controlled self-assembly (SA) of proteins offers the possibility to tune their properties or to create new materials. Herein, we present the synthesis of a modified human insulin (HI) with two distinct metal-ion binding sites, one native, the other abiotic, enabling hierarchical SA through coordination with two different metal ions. Selective attachment of an abiotic 2,2′-bipyridine (bipy) ligand to HI, yielding HI–bipy, enabled ZnII-binding hexamers to SA into trimers of hexamers, [[HI–bipy]6]3, driven by octahedral coordination to a FeII ion. The structures were studied in solution by small-angle X-ray scattering and on surfaces with AFM. The abiotic metal ligand had a higher affinity for FeII than ZnII ions, enabling control of the hexamer formation with ZnII and the formation of trimers of hexamers with FeII ions. This precise control of protein SA to give oligomers of oligomers provides nanoscale structures with potential applications in nanomedicine.

General information

State: Published

Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry, University of Copenhagen, Lund University, Novo Nordisk A/S


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Publication date: 2016

Main Research Area: Technical/natural sciences
Construction of Insulin 18-mer Nanoassemblies Driven by Coordination to Iron(II) and Zinc(II) Ions at Distinct Sites

Controlled self-assembly (SA) of proteins offers the possibility to tune their properties or to create new materials. Herein, we present the synthesis of a modified human insulin (HI) with two distinct metal-ion binding sites, one native, the other abiotic, enabling hierarchical SA through coordination with two different metal ions. Selective attachment of an abiotic 2,2′-bipyridine (bipy) ligand to HI, yielding HI–bipy, enabled ZnII-binding hexamers to SA into trimers of hexamers, \([\text{HI–bipy}]_6^3\), driven by octahedral coordination to a FeII ion. The abiotic metal ligand had a higher affinity for FeII than ZnII ions, enabling control of the hexamer formation with ZnII and the formation of trimers of hexamers with FeII ions. This precise control of protein SA to give oligomers of oligomers provides nanoscale structures with potential applications in nanomedicine.
Iron porphyrin, hemin (Fig. 1A), is the active core in cytochromes, haemoglobin and myoglobin, and enzymes such as the peroxidases. These metalloproteins are engaged in respiratory electron transfer, oxygen transport and storage, and enzyme catalysis in the biosynthesis of a range of metabolites. Hemin itself also acts as catalyst in electrochemical reduction of dioxygen and other small inert molecules such as nitrogen monoxide, and in electrochemiluminescent detection of dioxygen, peroxide, DNA, and proteins. N-n interactions of hemin with carbon materials have been broadly studied. Hemin on noble metalsurfaces has been prime targets in high-resolution STM but much less used in applied contexts such as biosensors and drug delivery. How hemin molecules interact with noble metal surfaces offers, however, other challenges in nanoscale and single-molecule science. We have studied hemin adsorption on well-defined single-crystal Au(111)-electrode surfaces using electrochemistry combined with scanning tunnelling microscopy under electrochemical control. Hemin gives two voltammetric peaks assigned to adsorbed monomers and dimmers (Fig. 1B). In situ STM shows that hemin self-assembles in ordered monolayers through non-covalent adsorption, as the reconstruction of the Au-(111) surface underneath the hemin layer is clearly visible (Fig. 1C).
Extracellular polymeric substances play roles in extracellular electron transfer of Shewanella oneidensis MR-1

It is well known that microorganism is surrounded by extracellular polymeric substances (EPS) which include polysaccharides, proteins, glycoproteins, nucleic acids, phospholipids, and humic acids. However, previous studies on microbial extracellular electron transfer (EET) are conducted on cells without extracting EPS or cells collected from log stage or early-steady stage cultures with little EPS. Therefore, microbial cells are believed in contact directly with each other or electrode. Such attempt apparently ignored the role of EPS in microbial EET, even though many components of EPS, such as DNA, humic acids and some proteins, are electrochemically active or semiconductive. Herein, we report experimental evidences of EPS role on EET for Shewanella oneidensis MR-1.

Atomic force microscopy clearly showed that the cell surface was cleaned and few EPS could be observed on MR-1 after the extraction (Figure 1.a and 1.b). Comparing to cells in control group, MR-1 treated at 38 °C for EPS extraction showed different electrochemical characterizations as revealed by differential pulse voltammetry (Figure 1.c). EPS extracted from MR-1 also was proved to be electrochemically active. The present study indicated that EPS play important roles in EET of MR-1.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Metalloprotein Chemistry and Engineering, Organic Chemistry, Chinese Academy of Sciences
Authors: Xiao, Y. (Intern), Zhang, E. (Ekstern), Christensen, H. E. M. (Intern), Zhang, J. (Intern), Zhao, F. (Ekstern)
Number of pages: 1
Publication date: 2016
Event: Abstract from 3rd European Meeting of the International Society for Microbial Electrochemistry and Technology (EU-ISMET 2016), Rome, Italy.
Flavins mediate extracellular electron transfer in Gram-positive Bacillus megaterium strain LLD-1

Electrochemically active microorganisms are microbes which can transfer electrons from cell to extracellular electron acceptors such as minerals, contaminants, electrodes, etc., and these processes are defined as extracellular electron transfer. In this study, we isolated and identified a new electrochemically active strain of Bacillus megatherium strain LLD-1, and its extracellular electron transfer mechanism was demonstrated by cyclic voltammetry (CV), differential pulse voltammetry (DPV), HPLC, and chronoamperometric.

The CV and DPV showed that a redox peaks ascribing to membrane proteins was found in the strain LLD-1; another redox peaks observed in cell and supernatant were ascribed to flavins. 74% increment of voltage generation in LLD-1 inoculated microbial fuel cell (MFC) can be made by adding extra 0.1 μM flavins mixture solution.

Graphene paper based bioelectrodes for enzymatic biofuel cells

We aim at developing bioelectrodes for enzymatic biofuel cells, where sustainable and renewable enzymes are used for catalyzing the oxidation and reduction of fuel molecules. Here glucose is chosen as fuel molecule and glucose oxidase (GOx) is target enzyme which catalyzes the oxidation of glucose. Due to its large surface area, good electronic conductivity and biocompatibility, 3-dimensional graphene paper is used as supporting electrode material to accommodate GOx. In addition, graphene paper is flexible with good mechanic strength and an ideal fit for bioelectrodes. The graphene paper based GOx electrode is made through formation of graphene oxide, graphene paper and immobilization of GOx on the graphene paper. The prepared bioelectrodes have been measured by electrochemistry and scanning electron microscopy (SEM). Cyclic voltammetry show clearly electrocatalytic signals for oxidation of glucose. This indicates that the enzyme has been successfully immobilized and is actively consuming glucose while transferring electrons to the graphene paper-GOx bioanode. Stability and efficiency of the bioelectrodes are under investigation.

Graphene Supported Au-Pt Core-Shell Catalyst: Electrocatalysis of Formic Acid Oxidation

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry
Authors: Seselj, N. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
Publication date: 2016
High Catalysis Activity of Cu$_2$O Microcrystals to the Electrochemiluminescence of Luminol and H$_2$O$_2$

Cuprous oxide (Cu$_2$O) is a classical p-type semiconductor with a direct band gap of 2.17 eV, which is widely used for solar energy conversion, CO oxidation, and photo catalytic water splitting for the low cost and environmental friendliness. For the energy band positions are favorable to the hydrogen evolution and oxygen evolution potentials, Cu$_2$O materials also catalyze the reduction of hydrogen peroxide (H$_2$O$_2$), which is a critical molecule in the bodies’ metabolism processes or the industrial catalysis reactions. To improve detection sensitivity of H$_2$O$_2$, people have composed Cu$_2$O materials with Ag nanoparticles or graphene nanosheets, which are sophisticated and cost. Herein, we use the electrochemiluminescence (ECL) method to improve the sensitivity of the reaction catalyzed by Cu$_2$O microcrystals. As shown by Figure 1A, the ECL reaction of H$_2$O$_2$ and luminol catalyzed by Cu$_2$O octahedra (Figure 1B) is strong at the potential of – 0.2 V (vs. Ag/AgCl). And the corresponding current of the reaction is not obvious (Figure 1A, inset). We also check the effect of copper ions (Cu$^{2+}$) to the ECL reaction, and there is much lower catalytic activity to the ECL reaction by Cu$^{2+}$ ions. It indicates that Cu$_2$O semiconductor microcrystal possess the good catalytic performance to this ECL reaction, which is important to develop the high-efficient and low-cost biosensors.

Laccase-3D graphene as catalysts for oxygen reduction in biocathodes

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry
Authors: Shen, F. (Intern), Werchmeister, R. M. L. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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http://www.sustain.dtu.dk/

Molecular Assembly of Hemin on Single-Crystal Au(111)-electrode Surfaces

Iron porphyrin, hemin, is the active core in cytochromes, haemoglobin and myoglobin, and enzymes such as the peroxidases. These metalloproteins are engaged in respiratory electron transfer, oxygen transport and storage, and enzyme catalysis in the biosynthesis of a range of metabolites. Hemin itself also acts as catalyst in electrochemical reduction of dioxygen and other small inert molecules such as nitrogen monoxide, and in electrochemiluminescent detection of dioxygen, peroxide, DNA, and proteins. n-n interactions of hemin with carbon materials have been broadly studied. Hemin on noble metal surfaces has been prime targets in high-resolution STM but much less used in applied contexts such as biosensors and drug delivery. How hemin molecules interact with noble metal surfaces offers, however, other challenges in nanoscale and single-molecule science. We have studied hemin adsorption on well-defined single-
crystal Au(111)-electrodesurfaces using electrochemistry combined with scanning tunnelling microscopy under
electrochemical control. Hemin gives two voltammetric peaks assigned to adsorbed monomers and dimmers (Fig. 1A). In
situ STM shows that hemin self-assembles in ordered monolayers through non-covalent adsorption, as the reconstruction
of the Au-(111) surface underneath the hemin layer is clearly visible (Fig. 1B).

Quinone-Enriched Gold Nanoparticles in Bioelectrochemistry and Charge Storage
We are aiming at the development of a general electrochemical platform suitable for multifarious investigations of biogenic
materials. The new platform can be attained by grafting organic/metal hybrids with quinone functionality. In-house made
and customized anthraquinone derivatives (with linking groups ranging from thiophenes to thiols) were chosen as model
compounds for linking together bulk quantities of gold nanoparticles and providing desired functionality. Anthraquinone
thiophene and thiol derivatives were synthetized via Sonogashira coupling-type reactions. The synthetic pathways for
merging gold nanoparticles with resultant anthraquinones include one-pot microwave assisted synthesis or after-mixing of
separately prepared gold nanoparticles with selected compounds. The quinone-enriched gold nanoparticles can be
transferred onto different electrode surfaces, thus enabling facile manufacturing of functional electroactive films.
Preliminary electrochemical investigations are indicative that quinone function is retained. The films can be utilized in
broad energy related applications. Enzymes immobilized on the crafted new electrode materials can act as cathodes with
"built-in" mediator for biofuel cells, or without any modification as anodes in putative and real charge storage devices.
Moreover, the new anthraquinone derivatives offer interesting perspectives related with molecular electronics.

Side Effect of Good's Buffers on Optical Properties of Gold Nanoparticle Solutions
In search of fluorescent nanoclusters (NCs) for bioimaging, several methods of synthesis have been attempted.
Particularly, formation of gold NCs (AuNCs) during synthesis of gold nanoparticles (AuNPs) using Good's buffers was
reported based on the optical properties of the reactions mixtures. Here we chose the Good's buffers 2-(N-
morpholino)ethanesulfonic acid (MES), 3-(N-morpholino)propanesulfonic acid (MOPS) and 4-(N-
morpholino)butanesulfonic acid (MOBS) as [AuCl4]- reducing agents. Resulting AuNP solutions were subjected to
electrochemical investigations along with UV-vis and fluorescence spectroscopy. Distinct absorption features at ca. 290
and 360 nm and fluorescence emission in the 408-484 nm range are observed in filtered AuNP-free solutions.
Electrochemical oxidation of these buffers generates similar optical properties, suggesting that the degradation products of
the buffers contribute to the optical properties of AuNP solutions. This work indicates deeper evaluation of fluorescence
signals based on metal NPs or NCs is needed.
The Au-S bond and SAM-protein contact in long-range electron transfer of pure and biomimetic metalloproteins via functionalized alkanethiol linkers

Interfacial electrochemical electron transfer (ET) of redox metalloproteins is long established. For the proteins to retain full ET or enzyme activity, modification of the electrode surfaces, say gold surfaces by self-assembled molecular monolayers (SAMs) is nearly always needed, where functionalized alkanethiols have emerged as core linkers. We have studied molecular linking in the long-range ET (LRET) processes in detail using electrochemistry, in situ STM and AFM, and electronic structure computations. A focus is the electronic structure of the Au-S link and the SAM packing. We have disentangled a wealth of data to identify the nature of the crucial Au-S contact, all suggesting prevalence of a Au(0)-thiyl radical unit. Molecular packing is further determined by the SAM molecular structure and involves binding either to Au-atoms mined out of the surface or directly to a flat surface. We illustrate this by high-resolution in situ STM of straight, branched, and chiral alkanethiols on Au(111)-electrode surfaces. We discuss next LRET of two SAM immobilized multi-copper enzymes, nitrite reductase and laccase, mapped to single-molecule resolution by in situ STM and AFM. The voltammetry is exceedingly sensitive to the structure of the thiol-based SAM molecules, testifying to the crucial importance of SAM packing and Au-S binding, and of the SAM link to the protein. Some of the subtleties are illustrated simpler by similar size (5-6 nm) nanoparticles (NPs). Biomimetic NPs must possess a certain degree of electronic structure sophistication. At the molecular scale this requirement is met by NPs of the renowned mixed-valence Prussian Blue (PB) assembled on Au(111)-electrode surfaces via functionalized alkanethiols. PBNP SAMs show LRET comparable to metalloproteins. Alkanethiols with different terminal groups exhibit, further intriguing LRET differences, reflecting other subtleties. We discuss the molecular LRET mechanisms and the intrinsic conductivity of the PBNPs.
Voltammetry and Molecular Assembly of G-quadruplex DNAzyme on Single-crystal Au(111)-electrode Surfaces – Hemin as an Electrochemical Intercalator

DNA quadruplexes (qs's) are a class of “non-canonical” oligonucleotides (OGNs) composed of stacked guanine (G) quartets generally stabilized by monovalent cations. Metal porphyrins selectively bind to G-qs complexes to form DNAzyme, which can exhibit peroxidase and other catalytic activity similar to heme group metalloenzymes. In the present study we investigate the electrochemical properties and the structure of DNAzyme monolayers on single-crystal Au(111)-electrode surfaces using cyclic voltammetry and scanning tunnelling microscopy under electrochemical potential control (in situ STM). The target DNZyme is formed from a single-strand OGN with 12 guanines and iron (III) porphyrin IX (hemin), and assemblies on Au(111) by the mercapto alkyl linker. The DNAzyme monolayers exhibit a strong pair of redox peaks at 0.0 V (NHE) at pH 7 in acetate buffer, shifted positively by about 50 mV compared to free hemin physisorbed on the Au(111). The voltammetric signal of DNZyme is enhanced 15 times, indicative that hemin is strongly bound to the immobilized 12G-qs and in well-defined orientation favorable for interfacial ET with a rate constant of 6.0 s⁻¹. The G-quartet structures with a size of 1.6 ± 0.2 nm are observed under in situ STM.

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Authors: Engelbrekt, C. (Intern), Nazmutdinov, R. R. (Ekstern), Yan, J. (Ekstern), Zinkicheva, T. (Ekstern), Mao, B. (Ekstern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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Development of 3 D-graphene for Biofuel Cells

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DNA bases assembled on the Au(110)/electrolyte interface: A combined experimental and theoretical study

Among the low-index single-crystal gold surfaces, the Au(110) surface is the most active toward molecular adsorption and the one with fewest electrochemical adsorption data reported. Cyclic voltammetry (CV), electrochemically controlled scanning tunneling microscopy (EC-STM), and density functional theory (DFT) calculations have been employed in the present study to address the adsorption of the four nucleobases adenine (A), cytosine (C), guanine (G), and thymine (T), on the Au(110)-electrode surface. Au(110) undergoes reconstruction to the (1 × 3) surface in electrochemical environment, accompanied by a pair of strong voltammetry peaks in the double-layer region in acid solutions. Adsorption of the DNA bases gives featureless voltammograms with lower double-layer capacitance, suggesting that all the bases are chemisorbed on the Au(110) surface. Further investigation of the surface structures of the adlayers of the four DNA bases by EC-STM disclosed lifting of the Au(110) reconstruction, specific molecular packing in dense monolayers, and pH dependence of the A and G adsorption. DFT computations based on a cluster model for the Au(110) surface were performed to investigate the adsorption energy and geometry of the DNA bases in different adsorbate orientations. The optimized geometry is further used to compute models for STM images which are compared with the recorded STM images. This has provided insight into the physical nature of the adsorption. The specific orientations of A, C, G, and T on Au(110) and the nature of the physical adsorbate/surface interaction based on the combination of the experimental and theoretical studies are proposed, and differences from nucleobase adsorption on Au(111)-and Au(100)-electrode surfaces are discussed.
Electrocatalysis of chemically synthesized noble metal nanoparticles on carbon electrodes

Noble metal nanoparticles (NPs), such as platinum (Pt) and palladium (Pd) NPs are promising catalysts for dioxygen reduction and oxidation of molecules such as formic acid and ethanol in fuel cells. Carbon nanomaterials are ideal supporting materials for electrochemical catalysts due to their good conductivity, chemical inertness and low cost. Improvement of catalytic efficiency and stability of the NPs is, however, essential for their wider applications in electrochemical energy conversion/storage. The activities of noble metal catalysts depend not only on their size, composition, and shapes but also on their interfacial interaction with the supporting electrodes. In this work we aim at chemical production of size and shape controlled, specifically 22 nm cubic Pd NPs, and further understanding of the Pd NPs as electrocatalysts at the nanometer scale using both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) which have proved to be highly efficient techniques to map the in situ structures of selfassembled molecular monolayers at molecular or sub-molecular resolution. Electrocatalysis of the Pd NPs immobilized on atomically flat, highly oriented pyrolytic graphite (HOPG) will be investigated by electrochemical SPM. This study offers promise for development of new high-efficiency catalyst types with low-cost for fuel cell technology.
Facile synthesis of starch-scaffolded bimetallic Au-Pt nanostructure and electrocatalysis

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Graphene-supported platinum catalysts for fuel cells

Increasing concerns with non-renewable energy sources drive research and development of sustainable energy technology. Fuel cells have become a central part in solving challenges associated with energy conversion. This review summarizes recent development of catalysts used for fuel cells over the past 15 years. It is focused on polymer electrolyte membrane fuel cells as an environmentally benign and feasible energy source. Graphene is used as a promising support material for Pt catalysts. It ensures high catalyst loading, good electrocatalysis and stability. Attention has been drawn to structural sensitivity of the catalysts, as well as polymetallic and nanostructured catalysts in order to improve the oxygen reduction reaction. Characterization methods including electrochemical, microscopic and spectroscopic techniques are summarized with an overview of the latest technological advances in the field. Future perspective is given in a form of Pt-free catalysts, such as microbial fuel cells for long-term development.

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Intermixed Adatom and Surface-Bound Adsorbates in Regular Self-Assembled Monolayers of Racemic 2-Butanethiol on Au(111)

In situ scanning tunneling microscopy combined with density functional theory molecular dynamics simulations reveal a complex structure for the self-assembled monolayer (SAM) of racemic 2-butanethiol on Au(111) in aqueous solution. Six adsorbate molecules occupy a (10×3)R30° cell organized as two RSAuSR adatom-bound motifs plus two RS species bound directly to face-centered-cubic and hexagonally close-packed sites. This is the first time that these competing head-group arrangements have been observed in the same ordered SAM. Such unusual packing is favored as it facilitates SAMs with anomalously high coverage (30 %), much larger than that for enantiomerically resolved 2-butanethiol or secondary-branched butanethiol (25 %) and near that for linear-chain 1-butanethiol (33 %).

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Scopus rating (2015): SJR 1.334 SNIP 0.912 CiteScore 3.21
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.362 SNIP 0.905 CiteScore 3.12
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 1.442 SNIP 0.948 CiteScore 3.22
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 1.763 SNIP 0.955 CiteScore 3.24
ISI indexed (2012): ISI indexed yes
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Scopus rating (2011): SJR 1.719 SNIP 1.05 CiteScore 3.37
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 1.872 SNIP 1.031
Web of Science (2010): Indexed yes
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Scopus rating (2009): SJR 1.91 SNIP 1.12
Porous poly(perfluorosulfonic acid) membranes for alkaline water electrolysis

Poly(perfluorosulfonic acid) (PFSA) is one of a few polymer types that combine excellent alkali resistance with extreme hydrophilicity. It is therefore of interest as a base material in separators for alkaline water electrolyzers. In the pristine form it, however, shows high cation selectivity. To increase its ion conductivity in aqueous KOH, a method for the preparation of porous PFSA membranes was developed. It was based on an approach where PFSA was co-cast with poly(vinylpyrrolidone) (PVP) at different ratios to give transparent and colorless blend membranes. The PVP was subsequently dissolved and washed out and the obtained porous materials allowed for swelling to reach water contents up to \( \lambda = 85 \) [H2O] [−SO3K]−1. After equilibration in 22 wt% aqueous KOH, ion conductivity of 0.2 S cm−1 was recorded for this membrane type at room temperature, which is significantly higher than 0.01 S cm−1 for the unmodified membrane. The technological feasibility was demonstrated by testing the membranes in an alkaline water electrolysis cell with encouraging performance.
The SAMENS Method for Gold Nanostructure Syntheses: Green Synthesis and Electrocatalysis

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Authors: Engelbrekt, C. (Intern), Seselj, N. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)

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Tuning the composition of metastable $\text{Co}_x\text{Ni}_y\text{Mg}_{100-x-y}(\text{OH})(\text{OCH}_3)$ nanoplates for optimizing robust methane dry reforming catalyst

Finding controllable, low-cost, and scalable ways to generate Ni-based catalysts is the bottleneck for methane dry reforming catalyst design. A new method for generating trimetallic $\text{Co}_x\text{Ni}_y\text{Mg}_{100-x-y}$O solid solution platelets enclosed by (111) facets has been developed from the topotactic pyrolysis of the metastable precursor $\text{Co}_x\text{Ni}_y\text{Mg}_{100-x-y}(\text{OH})(\text{OCH}_3)$ derived from solvothermal synthesis. The catalyst composition and reaction conditions have been modulated to achieve maximum coke resistance and catalyst stability. Long-term stability for 1000 h time on stream at 800°C has been achieved for the optimized $\text{Co}_{0.075}\text{Ni}_{7.425}\text{Mg}_{92.5}$O catalyst. The role of Co in the catalyst has been disclosed through kinetic measurements and detailed characterization of the spent catalysts. Co is enriched on the Co–Ni alloy surface under reforming conditions and accelerates the gasification of coke intermediates. Co also enhances the chemisorption of oxygen and reduces the activation energy for methane fragmentation, which is the rate-determining step for the overall reaction.
Adsorption Dynamics and Self-Assembled L-cysteine on Au(100)

As the only amino acid with a functional thiol group, L-cysteine offers a strong perspective both for binding to gold and other metals, and for gentle immobilization of biomolecules. Binding to single-crystal, atomically planar surfaces offers the additional perspective that bound L-cysteine can be structurally mapped at the single-molecule level. In this work, we have followed the adsorption of L-cysteine on single-crystal Au(100) by measuring the electrode potential dynamics during the adsorption process. In situ STM revealed the structure of the self-assembled ordered layers. The molecular assemblies were studied through simulated STM image contrast based on density functional theory (DFT) including solvation effects. The adsorption kinetics showed clearly a complex pattern with at least one intermediate state. The modelling disclosed details of the interaction of all functional groups with the Au(100) substrate.

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Organisations: Department of Chemistry, NanoChemistry, Kazan National Research Technological University, Xiamen University
Authors: Engelbrekt, C. (Intern), Nazmutdinov, R. R. (Ekstern), Yan, J. (Intern), Zinkicheva, T. T. (Ekstern), Mao, B. (Ekstern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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Chemical Production of Graphene Catalysts for Electrochemical Energy Conversion

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Controlling the stereochemistry and regularity of butanethiol self-assembled monolayers on Au(111)
The rich stereochemistry of the self-assembled monolayers (SAMs) of four butanethiols on Au(111) is described, the SAMs containing up to 12 individual C, S, or Au chiral centers per surface unit cell. This is facilitated by synthesis of enantiomerically pure 2-butanethiol (the smallest unsubstituted chiral alkanethiol), followed by in situ scanning tunneling microscopy (STM) imaging combined with density functional theory molecular dynamics STM image simulations. Even though butanethiol SAMs manifest strong headgroup interactions, steric interactions are shown to dominate SAM structure and chirality. Indeed, steric interactions are shown to dictate the nature of the headgroup itself, whether it takes on the adatom-bound motif RS•Au(0)S•R or involves direct binding of RS• to face-centered-cubic or hexagonal-close-packed sites. Binding as RS• produces large, organizationally chiral domains even when R is achiral, while adatom binding leads to rectangular plane groups that suppress long-range expression of chirality. Binding as RS• also inhibits the pitting intrinsically associated with adatom binding, desirably producing more regularly structured SAMs.

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Dynamics study of green AuNP formation and their basis for Au-Pt core-shell nanostructure synthesis

The SAMENS method (saccharide-based approach to metallic nanostructure synthesis) is a synthesis platform for metallic nanostructures. The method has been developed since 2008 and can produce nanostructures of various sizes, shapes and compositions. Recently, a new methodology for studying the details of nanoparticle formation has been...
developed employing readily available electrochemical and optical techniques. The aim is to understand which parameters control the growth and shape and at which stages of the synthesis. The gold nanoparticles (AuNPs) studied are further used as seeds for size controlled AuNPs and Au - Pt core - shell NPs with an atomically thin Pt shell.

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**Graphene controlled H- and J-stacking of perylene dyes into highly stable supramolecular nanostructures for enhanced photocurrent generation.**

We report a new method for controlling H- and J-stacking in supramolecular self-assembly. Graphene nanosheets act as structure inducers to direct the self-assembly of a versatile organic dye, perylene into two distinct types of functional nanostructures, i.e. one-dimensional nanotubes via J-stacking and two-dimensional branched nanobuds through H-stacking. Graphene integrated supramolecular nanocomposites are highly stable and show significant enhancement of photocurrent generation in these two configurations of photosensing devices, i.e. solid-state optoelectronic constructs and liquid-junction solar cells.

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Authors: Gan, S. (Intern), Zhong, L. (Ekstern), Engelbrekt, C. (Intern), Zhang, J. (Intern), Han, D. (Ekstern), Ulstrup, J. (Intern), Chi, Q. (Intern), Niu, L. (Ekstern)
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Green synthesis and structural control of metal and mineral nanostructures

Nanomaterials are widely used in modern technology, especially as catalysts in energy technology. Nanocatalysts are often prepared from expensive elements that constitute a large part of the total device cost. A critical component in the successful implementation of sustainable energy technology is efficiency which in large part comes down to the efficiency of the catalyst. Global issues arising from the use and reliance on fossil fuels urges the transition to sustainable alternatives and the development of new highly efficient nanomaterials. The efficiency depends on structure so controlling size, shape and composition at the atomic level is essential. To this adds low cost if massive use is anticipated. In this work, nanostructures of gold, platinum/gold, platinum/palladium, clinoatacamite (Cu₂(OH)₃Cl), cupric oxide and gold/titanium dioxide were synthesized and broadly characterized, their formation mechanisms studied, and their application as catalysts in relevant systems tested. Solution synthesis of nanomaterials offers large-scale, mild production but control of size, shape and composition is often challenging. This may be improved by expanding the understanding of the complex processes of nanoparticle formation which, however, entails the development of new methods. Two approaches to the advancement of solution synthesis of gold nanomaterials for energy technology were exploited, namely the development of techniques to study nanoparticle formation and the synthesis of active, composite nanomaterials. In the first approach, time-resolved chronopotentiometry, pH, conductivity and turbidity, and ultraviolet-visible light spectroscopy were employed to follow the green synthesis of gold nanoparticles. Several distinct phases were observed with all techniques providing a broad picture of the complex processes. Strong indications of sequential reduction were found and details about ligands and surface immobilized molecules disclosed. This platform is a widely available alternative to traditionally used synchrotron techniques. In the second approach, systematic efforts toward size and shape control of gold nanostructures provided controlled synthesis of not only spherical gold nanoparticles of 8-80 nm but also graphene oxide templated preparation of flat, ring-shaped gold nanostructures up to 1 μm in diameter mainly exposing (111) facets. Increased efficiency of new platinum nanocatalysts was attempted by two parallel strategies. One entailed avoiding inactive bulk platinum using a gold core and leaving only vi an atomically thin platinum shell. The specific catalytic activity of this nanocomposite will be studied in the future. The other strategy was to alloy platinum with a cheaper element, i.e. palladium, while retaining high activity. Supported PdPt alloy nanoparticles were successfully prepared and showed promising performance as catalysts in direct methanol and formic acid fuel cells. Catalysts made from earth-abundant elements may provide other low-cost alternatives to traditional, scarce and expensive catalysts. This may be achieved through niche applications and nanoscale engineering. Copper mineral nanoparticles were prepared and studied for this purpose. A buffered synthesis offering the preparation of phase-pure clinoatacamite Cu₂(OH)₃Cl and tenorite CuO by controlling pH was developed. Detailed crystallographic characterization was obtained by combining X-ray diffraction and infrared spectroscopy. The synthesis of CuO was further optimized and the flat, rod-shaped nanostructures applied as heterogeneous catalysts for oxidative dehydrogenation reactions. High activity and good reusability was found and the potential of this noble metal-free system will be explored further. Solar energy is appealing as a plentiful and free energy source. A plasmonic photoelectrocatalytic system was prepared to utilize visible light by incorporating gold nanoparticles in titanium dioxide. The composite material showed improved optical properties compared to pure titanium dioxide and preliminary catalytic tests were promising.

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Nanoporous gold assembly of glucose oxidase for electrochemical biosensing

Nanoporous gold (NPG) is composed of three-dimensional (3D) bicontinuous nanostructures with large surface area. Nano-channels inside NPG provide an ideal local environment for immobilization of enzyme molecules with expected stabilization of the protein molecules. In this work, glucose oxidase (GOx) has been brought to assemble on NPG via surface chemical reactions to form enzyme modified NPG nanomaterial with promising sensitivity for glucose detection. Cyclic voltammetry and single-potential step chronoamperometry (SPSC) are employed to study the electrochemical behavior of both bare and enzyme-modified NPG. Two redox mediators, p-benzoquinone (BQ) and ferrocenecarboxylic acid (FCA) are used to shuttle electrons between the enzyme redox center inside of GOx and the NPG electrode. Diffusion patterns at the functionalized NPG electrode are found significantly different from those on planar gold electrodes. This is mainly caused by internal 3D single crystal-like structures of NPG. Electrostatically neutral BQ mediator gives much higher voltammetric sensitivity than negatively charged FCA for GOx modified NPG electrodes. This study provides insight into the understanding of the intrinsic properties of NPG materials aiming at evolving enzymatic biosensors with high performance. © 2014 Elsevier Ltd.

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Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.349 SNIP 1.344 CiteScore 4.86
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.391 SNIP 1.482 CiteScore 4.59
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.435 SNIP 1.607 CiteScore 4.44
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.651 SNIP 1.592 CiteScore 3.99
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.621 SNIP 1.803 CiteScore 4.15
ISI indexed (2011): ISI indexed yes
Selective synthesis of clinoatacamite Cu$_2$(OH)$_3$Cl and tenorite CuO nanoparticles by pH control

Copper nanomaterials play a role as catalysts in sustainable energy technology and sensor devices. We present a one-pot synthesis for the selective preparation of phase-pure clinoatacamite (Cu$_2$(OH)$_3$Cl) and cupric oxide (CuO) nanoparticles by controlling the pH of the solution. The effect of pH on the phase of the product was systematically investigated utilizing 2-(N-morpholino)ethanesulfonic acid (MES) buffer. Here, the MES buffer was crucial for the synthesis. It not only allowed for selective synthesis by controlling pH but also guided the morphology of the CuO nanoparticles. In addition, it directed the growth of Cu$_2$(OH)$_3$Cl to provide pure clinoatacamite without the presence of related poly-morphs. The products were characterized by transmission electron microscopy, infrared spectroscopy, ultraviolet–visible light spectroscopy, X-ray powder diffraction (XRD), scanning transmission X-ray microscopy and atomic force microscopy. Infrared spectroscopy was essential for characterization of closely related polymorphs of Cu$_2$(OH)$_3$Cl indistinguishable by XRD. A plausible mechanism has been proposed and discussed for the formation of the CuO and Cu$_2$(OH)$_3$Cl nanostructures.

General information

State: Published
Organisations: Department of Chemistry, NanoChemistry, Centre for Catalysis and Sustainable Chemistry, X-ray Crystallography, Chinese Academy of Sciences
Authors: Engelbrekt, C. (Intern), Malcho, P. (Intern), Andersen, J. (Intern), Zhang, L. (Ekstern), Ståhl, K. (Intern), Li, B. (Ekstern), Hu, J. (Ekstern), Zhang, J. (Intern)
Number of pages: 12
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Article number: 2561
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Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 1.74 SJR 0.485 SNIP 0.555
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.569 SNIP 0.689 CiteScore 1.97
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.663 SNIP 0.868 CiteScore 2.17
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.749 SNIP 1.013 CiteScore 2.54
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 0.855 SNIP 1.03 CiteScore 2.56
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.09 SNIP 1.44 CiteScore 3.52
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.966 SNIP 1.248
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.977 SNIP 1.053
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.989 SNIP 1.138
Scopus rating (2007): SJR 0.873 SNIP 1.082
Scopus rating (2006): SJR 0.862 SNIP 1.242
Scopus rating (2005): SJR 0.805 SNIP 1.174
Scopus rating (2004): SJR 0.805 SNIP 1.332
Scopus rating (2003): SJR 0.564 SNIP 0.87
Scopus rating (2002): SJR 0.676 SNIP 1.226
Scopus rating (2001): SJR 0.503 SNIP 0.653
Scopus rating (2000): SJR 0.296 SNIP 0.409
Web of Science (2000): Indexed yes
Original language: English
Clinoatacamite, pH control, Green synthesis, FTIR, CuO, Cu 2 (OH) 3 Cl
DOIs:
10.1007/s11051-014-2562-4

Relations
Complexity of gold nanoparticle formation disclosed by dynamics study
Although chemically synthesized gold nanoparticles (AuNPs) from gold salt (HAuCl₄) are among the most studied nanomaterials, understanding the formation mechanisms is a challenge mainly due to limited dynamics information. A range of in situ methods with down to millisecond (ms) time resolution have been employed in the present report to monitor time-dependent physical and chemical properties in aqueous solution during the chemical synthesis. Chemical synthesis of AuNPs is a reduction process accompanied by release of ions and protons, and formation of solid particles. Dynamic information from redox potential, pH, conductivity, and turbidity of the solution enables distinct observation of reduction and nucleation/growth of AuNPs phases. The dynamics of the electrochemical potential shows that reduction of gold salt (HAuCl₄ and its hydrolyzed forms) occurs via intermediate [AuCl₂]⁻ to form Au atoms during the early stage of the synthesis process. pH- and conductivity-dynamics point further clearly to formation of coating layers on AuNPs and adsorbate exchange between MES and starch. © 2013 American Chemical Society.
Direct measurement and modulation of single-molecule coordinative bonding forces in a transition metal complex.

Coordination chemistry has been a consistently active branch of chemistry since Werner's seminal theory of coordination compounds inaugurated in 1893, with the central focus on transition metal complexes. However, control and measurement of metal-ligand interactions at the single-molecule level remain a daunting challenge. Here we demonstrate an interdisciplinary and systematic approach that enables measurement and modulation of the coordinative bonding forces in a transition metal complex. Terpyridine is derived with a thiol linker, facilitating covalent attachment of this ligand on both gold substrate surfaces and gold-coated atomic force microscopy tips. The coordination and bond breaking between terpyridine and osmium are followed in situ by electrochemically controlled atomic force microscopy at the single-molecule level. The redox state of the central metal atom is found to have a significant impact on the metal-ligand interactions. The present approach represents a major advancement in unravelling the nature of metal-ligand interactions and could have broad implications in coordination chemistry.

**General information**

State: Published
Organisations: NanoChemistry, Department of Chemistry, Department of Physics, Theoretical Atomic-scale Physics, Chalmers University of Technology, Chinese Academy of Sciences
Publication date: 2013
Main Research Area: Technical/natural sciences

**Publication information**

Journal: Nature Communications
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Article number: 2121
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Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 11.8 SJR 6.399 SNIP 2.995
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Dynamic Approach to the Study of Green Nanoparticle Formation

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Organic Chemistry
Authors: Engelbrekt, C. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
Number of pages: 2
Publication date: 2013
Event: Abstract from 14th International Symposium on Electroanalytical Chemistry, Changchun, China.
Main Research Area: Technical/natural sciences
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Relations
Activities:
Dynamic Approach to the Study of Green Nanoparticle Formation
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2013

Ion Transfer Voltammetry Associated with Two Polarizable Interfaces Within Water and Moderately Hydrophobic Ionic Liquid Systems

An electrochemical system composed of two polarizable interfaces (the metallic electrode|water and water|ionic liquid interfaces), namely two-polarized-interface (TPI) technique, has been proposed to explore the ion transfer processes between water and moderately hydrophobic ionic liquids (W|mL), typically 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C8mimC1C1N) and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (C6mimC1C1N). Within the classic four-electrode system, it is not likely that the ion transfer information at the W|mL interface can be obtained due to an extremely narrow polarized potential window (ppw) caused by these moderately hydrophobic ionic components. In this article, we show that TPI technique has virtually eliminated the ppw limitation based on a controlling step of concentration polarization at the electrode|water interface. With the aid of this technique, the formal ion transfer potential differences between C1C1N− and Cnmim+ (n=6, 8) were accurately determined for 356 mV and 420 mV at a corresponding interface (W|C6mimC1C1N and W|C8mimC1C1N). Besides, this technique is used to monitor electrochemical polarization at the two W|mL systems, which exhibits an adaptable polarizability (i.e., a conversion from a nonpolarized interface to a polarized interface). Some of the typical anion transfers at the W|C8mimC1C1N interface have also been investigated, as they are particularly important for ion extraction. The experimental results indicate that this facile TPI technique offers a general avenue to explore ion transfer in multifarious biphasic systems.

General information
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Organisations: Department of Chemistry, NanoChemistry, Chinese Academy of Sciences
On the Hopping Efficiency of Nanoparticles in the Electron Transfer across Self-Assembled Monolayers

Redox reactions of solvated molecular species at gold-electrode surfaces modified by electrochemically inactive self-assembled molecular monolayers (SAMs) are found to be activated by introducing Au nanoparticles (NPs) covalently bound to the SAM to form a reactive Au–alkanedithiol–NP–molecule hybrid entity. The NP appears to relay long-range electron transfer (ET) so that the rate of the redox reaction may be as efficient as directly on a bare Au electrode, even though the ET distance is increased by several nanometers. In this study, we have employed a fast redox reaction of surface-confined 6-(ferrocenyl) hexanethiol molecules and NPs of Au, Pt and Pd to address the dependence of the rate of ET through the hybrid on the particular NP metal. Cyclic voltammograms show an increasing difference in the peak-to-peak separation for NPs in the order Au.
Aquatic toxicology of engineered nanoparticles is challenged by methodological difficulties stemming partly from highly dynamic and poorly understood behavior of nanoparticles in biological test systems. In this paper scientific and technical challenges of testing not readily soluble nanoparticles in standardised algal growth inhibition tests are highlighted with specific focus on biomass quantification methods. This is illustrated through tests with TiO$_2$ and Au nanoparticles, for which cell-nanoparticle interactions and behavior was studied during incubation. Au NP coating layers changed over time and TiO$_2$ nanoparticle aggregation/agglomeration increased as a function of concentration. Three biomass surrogate measuring techniques were evaluated (coulter counting, cell counting in haemocytometer, and fluorescence of pigment extracts) and out of these the fluorometric methods was found to be most suitable. Background correction was identified as a key issue for biomass quantification, complicated by algae-particle interactions and nanoparticle transformation. Optimisation of the method is needed to reduce further particle interference on measurements.
Au-Biocompatible metallic nanostructures in metalloprotein electrochemistry and electrocatalysis

Molecular scale metallic nanoparticles coated by molecular monolayers and immobilized on single-crystal Au-electrode surfaces are efficient catalysts in metalloprotein voltammetry. Nanoparticles prepared by a new “green” method also exhibit strong electrocatalysis in both protein electrochemistry and fuel cell related processes. In this communication we highlight some recent observations and discuss their possible physical origins.

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry
Authors: Jensen, P. S. (Intern), Engelbrekt, C. (Intern), Sørensen, K. H. (Ekstern), Zhang, J. (Intern), Chi, Q. (Intern), Ulstrup, J. (Intern)
Pages: 13877-13882
Publication date: 2012
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Materials Chemistry
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BFI (2014): BFI-level 2
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Original language: English
TiO2, Au, Growth inhibition, Ecotoxicity, Guidelines
Electronic versions:
17435390_2E2012_2E710657.pdf
DOIs:
10.3109/17435390.2012.710657
Source: dtu
Source-ID: u::5804
Publication: Research - peer-review › Journal article – Annual report year: 2012
Bacterial biofilms investigated by atomic force microscopy and electrochemistry

Bacterial biofilms are aggregates of microorganisms in which cells adhere to each other and to a solid surface or an animal host cavity. Bacterial biofilms play important roles in human life, and cause serious harm for human society and huge economic losses. The complex composition of bacterial biofilms with EPS (Extracellular polymeric substances) includes proteins, polysaccharides, extracellular DNA (e-DNA), peptidoglycans, lipids and phospholipids. These substances play an important role in the initial adhesion of bacteria to the surface and maintenance of the biofilm structure. In my thesis, Atomic Force Microscopy (AFM) and electrochemistry have been applied to investigate three pathogenic medically important bacterial biofilms, i.e. Pseudomonas aeruginosa (cystic fibrosis pneumonia), Staphylococcus epidermidis (contamination of surgical catheters and indwelling equipment) and Streptococcus mutans (dental caries).

AFM was used to investigate the adhesion force on single live cell surfaces. Four different strains of Staphylococcus epidermidis in liquid aqueous environments were addressed. These strains were selected because of their special surface proteins related with the initial attachment on the surface. High-resolution AFM imaging showed no detectable differences among the four strains. Adhesion maps using hydrophobically modified tips compared with bare hydrophilic silicon nitride tips also showed small differences only. This indicates that hydrophobic effects are not the primary driving forces towards adhesion. Two chemical inhibitor compounds were found to have strong effects on the adhesion between the bare tips and the bacteria.

Secondly, AFM and electrochemistry were combined to study bacterial biofilm formation on Au(111)-surfaces, to determine the surface charge and growth pattern of Streptococcus mutans biofilms. Five redox probes were chosen for cyclic voltammetry, i.e. positively, \([\text{Ru(NH}_3\text{)}_6]^{3+/2+}\) and \([\text{Co(phen)}]^{3+/2+}\) and \([\text{Co(terpy)}]^{3+/2+}\); phen = 1,10-phenanthroline; terpy = 2,2',2"-terpyridine) and negatively charged, \([\text{Fe(CN)}_6]^{3-/4-}\), \([\text{IrCl}_6]^{3-/4-}\). The inhibition and voltammetric patterns showed that S. mutans biofilm are negatively charged. Addition of DNAase suggests that the negative charges to a large extent originate from DNA excreted by the biofilm.

Thirdly, AFM and electrochemistry were combined to study Streptococcus mutans biofilm formation on bare Au(111) and Au(111) modified by self assembled molecular monolayers (SAMs) of thiol-based molecules. Four SAM molecules were chosen for reductive desorption (RD). Two are long straight-chain thiols with either a hydrophobic or a hydrophilic terminal group, i.e. hexadecanethiol, \(\text{HS(CH}_2\text{)}_{15}\text{CH}_3\) and mercaptophexadecanoic acid, \(\text{HS(CH}_2\text{)}_{15}\text{COOH}\). Two others were the short rigid linker molecules L-cysteine and cysteamine. Strong RD peaks were obtained for all the four molecules both in PBS buffer at pH 7.4 and in 0.1M NaOH solution. Both AFM images and the electrochemical data show further, that the biofilms are bound more strongly to the hydrophobic surface than to the hydrophilic surfaces.

Finally, AFM was used to study two other kinds of bacteria, Pseudomonas aeruginosa and Pseudomonas putida, and their relationship with EPS. Different mutant strains were applied to investigate the roles of Pel and Psl polysaccharides and type IV pili during P. aeruginosa biofilm development. This study suggests that polysaccharides and e-DNA contribute to the biofilm development. Protein clusters were observed during P. putida biofilm formation, but we need further investigation to identify or distinguish the surface protein Lap A and Lap F. The combination of AFM and electrochemistry is a new approach to understand the bacterial biofilm/medium/bare or modified Au(111) interface. Future efforts aim at observing the live bacterial biofilms with high resolution and controlling the biofilm.
formation on SAM-modified Au(111)-surfaces by the combination of AFM and electrochemical characterization.

**General information**
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Organisations: Department of Chemistry, NanoChemistry
Authors: Hu, Y. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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Original language: English
Main Research Area: Technical/natural sciences
Electronic versions:
Yifan Hu Thesis.pdf
Source: dtu
Source-ID: u::3925
Publication: Research › Ph.D. thesis – Annual report year: 2012

**Characterizing the Kinetics of Nanoparticle-Catalyzed Reactions by Surface-Enhanced Raman Scattering**

**General information**
State: Published
Organisations: Department of Chemistry, NanoChemistry, Humboldt-University of Berlin, Technical University of Berlin
Authors: Joseph, V. (Ekstern), Engelbrekt, C. (Intern), Zhang, J. (Intern), Gernert, U. (Ekstern), Ulstrup, J. (Intern), Kneipp, J. (Ekstern)
Pages: 7592-7596
Publication date: 2012
Main Research Area: Technical/natural sciences

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Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 10.8 SJR 5.8 SNIP 2.104
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 5.958 SNIP 2.235 CiteScore 11.13
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 5.805 SNIP 2.309 CiteScore 10.84
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 5.681 SNIP 2.204 CiteScore 10.7
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 6.362 SNIP 2.338 CiteScore 10.55
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 6.062 SNIP 2.387 CiteScore 10.75
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Dynamic Studies of Green AuNP Formation by Electrochemical and Optical Techniques

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry
Authors: Engelbrekt, C. (Intern), Jensen, P. S. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
Publication date: 2012
Event: Poster session presented at 63rd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic.
Main Research Area: Technical/natural sciences
Electronic versions:
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Source: PublicationPreSubmission
Source-ID: 101973466
Publication: Research - peer-review › Poster – Annual report year: 2012

Electrochemical Single-Molecule AFM of the Redox Metalloenzyme Copper Nitrite Reductase in Action
We studied the electrochemical behavior of the redox metalloenzyme copper nitrite reductase (CNIR, Achromobacter xylosoxidans) immobilized on a Au(111)-electrode surface modified by a self-assembled cysteamine molecular monolayer (SAM) using a combination of cyclic voltammetry and electrochemically-controlled atomic force microscopy (in situ AFM). The enzyme showed no voltammetric signals in the absence of nitrite substrate, whereas a strong reductive electrocatalytic signal appeared in the presence of nitrite. Such a pattern is common in protein film and monolayer voltammetry and points to conformational changes in the enzyme upon substrate binding. Binding thus either improves the enzyme/electrode contact, or opens intramolecular electron-transfer channels between the redox center for electron inlet (a type I copper center) and the catalytic site for nitrite reduction (a type II copper center). The in situ AFM data are at the
level of the single CuNiR enzyme molecule. The voltammetric patterns were paralleled by a clear increase (swelling) of the molecular height when the electrochemical potential traversed the region from resting to the electrocatalytically active redox enzyme function in the presence of nitrite. No change in size was observed in the absence of nitrite over the same potential range. The enzyme size variation is suggested to offer clues to the broadly observed substrate triggering in metalloenzyme monolayer voltammetry.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Metalloprotein Chemistry and Engineering, Chinese Academy of Sciences
Authors: Hao, X. (Ekstern), Zhang, J. (Intern), Christensen, H. E. M. (Intern), Wang, H. (Ekstern), Ulstrup, J. (Intern)
Pages: 2919-2924
Publication date: 2012
Main Research Area: Technical/natural sciences

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Journal: ChemPhysChem
Volume: 13
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ISSN (Print): 1439-4235
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Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.81 SJR 1.264 SNIP 0.771
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.334 SNIP 0.912 CiteScore 3.21
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.362 SNIP 0.905 CiteScore 3.12
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 1.442 SNIP 0.948 CiteScore 3.22
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 1.763 SNIP 0.955 CiteScore 3.24
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 1.719 SNIP 1.05 CiteScore 3.37
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 1.872 SNIP 1.031
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 1.91 SNIP 1.12
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 2.153 SNIP 1.098
Scopus rating (2007): SJR 2.215 SNIP 1.129
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.008 SNIP 1.159
Web of Science (2006): Indexed yes
Electrochemical surface immobilization triggers intramolecular electron transfer in multi-centre redox metalloproteins: The di-heme protein cytochrome c4

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Kazan National Research Technological University
Authors: Chi, Q. (Intern), Nazmudtinov, R. (Ekstern), Bronshtein, M. (Ekstern), Zinkicheva, T. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Publication date: 2012
Event: Abstract from 63rd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic.
Main Research Area: Technical/natural sciences
Electronic versions:
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Invited talk
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2012

Interfacial electrochemical electron transfer in biology – Towards the level of the single molecule
Physical electrochemistry has undergone a remarkable evolution over the last few decades, integrating advanced techniques and theory from solid state and surface physics. Single-crystal electrode surfaces have been a core notion, opening for scanning tunnelling microscopy directly in aqueous electrolyte (in situ STM). Interfacial electrochemistry of metalloproteins is presently going through a similar transition. Electrochemical surfaces with thiol-based promoter molecular monolayers (SAMs) as biomolecular electrochemical environments and the biomolecules themselves have been mapped with unprecedented resolution, opening a new area of single-molecule bioelectrochemistry. We consider first in situ STM of small redox molecules, followed by in situ STM of thiol-based SAMs as molecular views of bioelectrochemical environments. We then address electron transfer metalloproteins, and multi-centre metalloenzymes including applied single-biomolecular perspectives based on metalloprotein/metallic nanoparticle hybrids.

General information
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Organisations: NanoChemistry, Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Hansen, A. G. (Intern), Jensen, P. S. (Intern), Salvatore, P. (Intern), Ulstrup, J. (Intern)
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Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 3.48 SJR 1.898 SNIP 0.885
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 2.02 SNIP 0.927 CiteScore 3.49
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.86 SNIP 0.871 CiteScore 3.19
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 2.328 SNIP 0.984 CiteScore 3.71
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 2.259 SNIP 0.914 CiteScore 3.67
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 2.264 SNIP 0.837 CiteScore 3.5
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 2.197 SNIP 0.795
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 2.131 SNIP 0.792
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 2.15 SNIP 0.79
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.115 SNIP 0.813
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.18 SNIP 0.849
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 2.108 SNIP 0.84
Scopus rating (2004): SJR 2.299 SNIP 0.887
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 2.32 SNIP 0.924
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 2.185 SNIP 0.945
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 2.154 SNIP 0.955
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 2.219 SNIP 0.94
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 2.456 SNIP 0.997
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Modeling and computations of the intramolecular electron transfer process in the two-heme protein cytochrome c4

The di-heme protein *Pseudomonas stutzeri* cytochrome c4 (cyt c4) has emerged as a useful model for studying long-range protein electron transfer (ET). Recent experimental observations have shown a dramatically different pattern of intramolecular ET between the two heme groups in different local environments. Intramolecular ET in homogeneous solution is too slow (>10 s) to be detected but fast (ms–μs) intramolecular ET in an electrochemical environment has recently been achieved by controlling the molecular orientation of the protein assembled on a gold electrode surface. In this work we have performed computational modeling of the intramolecular ET process by a combination of density functional theory (DFT) and quantum mechanical charge transfer theory to disclose reasons for this difference. We first address the electronic structures of the model heme core with histidine and methionine axial ligands in both low- and high-spin states by structure-optimized DFT. The computations enable estimating the intramolecular reorganization energy of the ET process for different combinations of low- and high-spin heme couples. Environmental reorganization free energies, work terms ("gating") and driving force were determined using dielectric continuum models. We then calculated the electronic transmission coefficient of the intramolecular ET rate using perturbation theory combined with the electronic wave functions determined by the DFT calculations for different heme group orientations and Fe–Fe separations. The reactivity of low- and high-spin heme groups was notably different. The ET rate is exceedingly low for the crystallographic equilibrium orientation but increases by several orders of magnitude for thermally accessible non-equilibrium configurations. Deprotonation of the propionate carboxyl group was also found to enhance the ET rate significantly. The results are discussed in relation to the observed surface immobilization effect and support the notion of conformationally gated ET.
Polycation Induced Potential Dependent Structural Transitions of Oligonucleotide Monolayers on Au(111)-Surfaces

We have studied self-assembled molecular monolayers (SAMs) of several 3′-C3-SH conjugated single-strand (ss) and double-strand (ds) 20-base oligonucleotides (ONs) immobilized on single-crystal, atomically planar Au(111)-electrode surfaces in the presence of the triply positively charged base spermidine (Spd). This cation binds strongly to the polyanionic ON backbone and stabilizes the ds-form relative to the ss-form. A combination of chemical ON synthesis, melting temperature measurements, cyclic voltammetry (CV), and in situ scanning tunneling microscopy (STM) in aqueous biological buffer under electrochemical potential control was used. Spd binding was found to increase notably the ds-ON melting temperature. CV displays capacitive features associated with ss- and ds-ON. A robust capacitive peak around −0.35 V versus saturated calomel electrode (SCE), specific to ds-ON and highly sensitive to base pair mismatches, was consistently observed. The peak is likely to be caused by surface structural reorganization around the peak potential and located close to reported peak potentials of several DNA intercalating or covalently tethered redox molecules reported as probes for long-range electron transfer.

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, University of Southern Denmark, University of Liverpool
Authors: Salvatore, P. (Intern), Karlsen, K. K. (Forskerdatabase), Hansen, A. G. (Intern), Zhang, J. (Intern), Nichols, R. J. (Ekstern), Ulstrup, J. (Intern)
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Scopus rating (2015): SJR 6.826 SNIP 2.632 CiteScore 12.81
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BFI (2014): BFI-level 2
Scopus rating (2014): SJR 6.273 SNIP 2.578 CiteScore 11.92
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 5.953 SNIP 2.455 CiteScore 11.38
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 6.141 SNIP 2.379 CiteScore 10.37
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
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Scopus rating (2011): SJR 5.447 SNIP 2.336 CiteScore 9.94
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Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 5.076 SNIP 2.132
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 4.883 SNIP 2.176
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 4.936 SNIP 2.116
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 5.023 SNIP 2.126
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 4.546 SNIP 2.22
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 4.284 SNIP 2.207
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 3.754 SNIP 2.178
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 3.267 SNIP 2.215
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 3.527 SNIP 2.346
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 3.449 SNIP 2.199
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 3.573 SNIP 2.224
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 3.56 SNIP 2.182

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Spontaneous and Fast Growth of Large-Area Graphene Nanofilms Facilitated by Oil/Water Interfaces

An efficient wet-chemical method based on soft interfacial self-assembly is developed for spontaneous, fast growth of large-area graphene nanofilms on various substrates. The graphene nanofilms produced show tunable optical properties and a highly reversible optoelectronic response. Complementary to chemical vapor deposition, this method could offer a fast, simple, and low-cost chemical strategy to produce graphene nanofilms.

General information
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Organisations: Department of Chemistry, NanoChemistry, State Key Laboratory of Electroanalytical Chemistry
Authors: Gan, S. (Intern), Zhong, L. (Ekstern), Wu, T. (Ekstern), Han, D. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern), Chi, Q. (Intern), Niu, L. (Intern)
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Web of Science (2018): Indexed yes
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Scopus rating (2016): CiteScore 17.79
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): CiteScore 18.5
Web of Science (2015): Indexed yes
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Scopus rating (2014): CiteScore 16.79
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): CiteScore 15.78
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 14.41
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): CiteScore 12.28
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
Voltammetry and single-molecule in situ scanning tunneling microscopy of laccases and bilirubin oxidase in electrocatalytic dioxygen reduction on Au(111) single-crystal electrodes

Laccases (E.C. 1.10.3.2) are multicopper oxidases catalytically active in the oxidation of diphenolics and related compounds by molecular dioxygen. The laccases contain a single-copper type I center and a trinuclear cluster of a single-copper type II and a dinuclear type III center. The oxidation of four equivalents of substrate near the type I copper and the sequential transfer of electrons to the trinuclear cluster are coupled with four-electron reduction of O₂ to H₂O at the latter site. Extensive efforts have been given to kinetic and structural characterization of numerous laccasés to elucidate the catalytic mechanism, where laccase (sub)monolayer voltammetry has been a core approach. In this report, we address voltammetry and electrocatalysis of O₂ reduction of (sub)monolayers of several laccases in new ways. These are based on the use of single-crystal, atomically planar bare Au(111)-electrode surfaces or surfaces modified by thiol-based self-assembled molecular monolayers. These well-defined surfaces enable introducing electrochemical scanning tunneling microscopy directly in aqueous biological media in which the enzymes are operative (in situ STM), to the level of resolution of the single enzyme molecule in electrocatalytic action. Enzyme-electrode electronic contact and intramolecular electron transfer triggered by the electrode potential or by O₂-substrate binding to the enzyme, followed at the single-molecule level, are the most important observations of this study. © 2011 American Chemical Society.
Scopus rating (2014): SJR 2.027 SNIP 1.448 CiteScore 5.08
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 2.134 SNIP 1.439 CiteScore 5.14
ISI indexed (2013): ISI indexed yes
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BFI (2012): BFI-level 1
Scopus rating (2012): SJR 2.514 SNIP 1.46 CiteScore 4.98
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Web of Science (2012): Indexed yes
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Scopus rating (2011): SJR 2.32 SNIP 1.457 CiteScore 4.92
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 2.438 SNIP 1.356
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 2.128 SNIP 1.417
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 1.856 SNIP 1.033
Web of Science (2008): Indexed yes
Web of Science (2007): Indexed yes
Web of Science (2006): Indexed yes
Web of Science (2005): Indexed yes
Web of Science (2004): Indexed yes
Web of Science (2003): Indexed yes
Web of Science (2002): Indexed yes
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Adhesive properties of Staphylococcus epidermidis probed by atomic force microscopy
Mapping of the surface properties of Staphylococcus epidermidis and of biofilm forming bacteria in general is a key to understand their functions, particularly their adhesive properties. To gain a comprehensive view of the structural and chemical properties of S. epidermidis, four different strains (biofilm positive and biofilm negative strains) were analyzed using in situ atomic force microscopy (AFM). Force measurements performed using bare hydrophilic silicon nitride tips disclosed similar adhesive properties for each strain. However, use of hydrophobic tips showed that hydrophobic forces are not the driving forces for adhesion of the four strains. Rather, the observation of sawtooth force–distance patterns on the surface of biofilm positive strains documents the presence of modular proteins such as Aap that may mediate cell adhesion. Treatment of two biofilm positive strains with two chemical inhibitor compounds leads to a loss of adhesion, suggesting that AFM could be a valuable tool to screen for anti-adhesion molecules.

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Center for Systems Microbiology, Department of Systems Biology, Universite Catholique de Louvain
Chain-Branching Control of the Atomic Structure of Alkanethiol-Based Gold–Sulfur Interfaces

Density functional theory structure calculations at 0 K and simulations at 300 K of observed high-resolution in situ scanning tunneling microscopy (STM) images reveal three different atomic-interface structures for the self-assembled monolayers (SAMs) of three isomeric butanethiols on Au(111): direct binding to the Au(111) surface without pitting, binding to adatoms above a regular surface with extensive pitting, and binding to adatoms with local surface vacancies and some pitting. Thermal motions are shown to produce some observed STM features, with a very tight energy balance controlling the observed structures. Variation of the degree of substitution on the α carbon is found to significantly change the relative energies for interaction of the different types of adatom structures with the surface, while the nature of the surface cell, controlled primarily by inter-adsorbate steric interactions, controls substrate reorganization energies and adsorbate distortion energies. Most significantly, by manipulating these features, chemical control of the adsorbate can produce stable interfaces with surface pitting eliminated, providing new perspectives for technological applications of SAMs.

General information
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Organisations: NanoChemistry, Department of Chemistry, Griffith University, University of Sydney
Authors: Wang, Y. (Ekstern), Chi, Q. (Intern), Zhang, J. (Intern), Hush, N. S. (Ekstern), Reimers, J. R. (Ekstern), Ulstrup, J. (Intern)
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Scopus rating (2016): CiteScore 13.18 SJR 7.368 SNIP 2.584
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Scopus rating (2014): SJR 6.273 SNIP 2.578 CiteScore 11.92
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 5.953 SNIP 2.455 CiteScore 11.38
ISI indexed (2013): ISI indexed yes
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Distinct roles of extracellular polymeric substances in Pseudomonas aeruginosa biofilm development
Bacteria form surface attached biofilm communities as one of the most important survival strategies in nature. Biofilms consist of water, bacterial cells and a wide range of self-generated extracellular polymeric substances (EPS). Biofilm formation is a dynamic self-assembly process and several distinguishable stages are observed during bacterial biofilm development. Biofilm formation is shown to be coordinated by EPS production, cell migration, subpopulation differentiation and interactions. However, the ways these different factors affect each other and contribute to community structural differentiation remain largely unknown. The distinct roles of different EPS have been addressed in the present report. Both Pel and Psl polysaccharides are required for type IV pilus-independent microcolony formation in the initial stages of biofilm formation by Pseudomonas aeruginosa PAO1. Both Pel and Psl polysaccharides are also essential for subpopulation interactions and macrocolony formation in the later stages of P. aeruginosa PAO1 biofilm formation. Pel and Psl polysaccharides have different impacts on Pseudomonas quinolone signal-mediated extracellular DNA release in P. aeruginosa PAO1 biofilms. Psl polysaccharide is more important than Pel polysaccharide in P. aeruginosa PAO1 biofilm formation and antibiotic resistance. Our study thus suggests that different EPS materials play distinct roles during bacterial biofilm formation.

General information
Dynamics of Green AuNP Formation and Their Application in Core-Shell Nanostructures

The formation of gold nanoparticles in our optimized synthesis is achieved through reduction of tetrachloroauric acid in 2-(N-morpholino)ethanesulphonic acid (MES) buffered glucose and stabilization by starch at room temperature. The formation has been followed by measuring the electrochemical potential, conductivity, pH, turbidity, UV-Vis extinction, core size and hydrodynamic diameter. The synthesized AuNPs have been employed as core particles in advanced core-shell structures with highly porous platinum nanoparticle coating or copper oxide shells. These hold potentials as effective catalysts in fuel cells and methanol reformers.

Electrochemically controlled self-assembled monolayers characterized with molecular and sub-molecular resolution

Self-assembled organization of functional molecules on solid surfaces has developed into a powerful and sophisticated tool for surface chemistry and nanotechnology. A number of reviews on the topic have been available since the mid-1990s. This perspective article aims to focus on recent development in the investigations of electronic structures and assembling dynamics of electrochemically controlled self-assembled monolayers (SAMs) of thiol containing molecules on gold surfaces. A brief introduction is first given and particularly illustrated by a Table summarizing the molecules studied, the surface lattice structures and the experimental operating conditions. This is followed by discussion of two major high-resolution experimental methods, scanning tunnelling microscopy (STM) and single-crystal electrochemistry. In Section 3, we briefly address choice of supporting electrolytes and substrate surfaces, and their effects on the SAM structures. Section 4 constitutes the major body of the article by offering some details of recent studies for the selected cases, including in situ monitoring of assembling dynamics, molecular electronic structures, and the key external factors determining the SAM packing. In Section 5, we give examples of what can be offered by theoretical computations for the detailed understanding of the SAM electronic structures revealed by STM images. A brief summary of the current applications of SAMs in wiring metalloproteins, design and fabrication of sensors, and single-molecule electronics is described in Section 6. In the final two sections (7 and 8), we discuss the current status in understanding of electronic structures and properties of SAMs in electrochemical environments and what could be expected for future perspectives.
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Scopus rating (2016): CiteScore 4.06 SJR 1.678 SNIP 1.117
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.771 SNIP 1.244 CiteScore 4.45
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.772 SNIP 1.253 CiteScore 4.29
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 1.715 SNIP 1.216 CiteScore 4.05
 ISI indexed (2013): ISI indexed yes
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Scopus rating (2012): SJR 1.916 SNIP 1.184 CiteScore 3.67
 ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 1.697 SNIP 1.203 CiteScore 3.6
 ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 1.802 SNIP 1.196
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 2.127 SNIP 1.369
Web of Science (2009): Indexed yes
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Scopus rating (2008): SJR 2.158 SNIP 1.211
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 1.84 SNIP 1.138
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 1.467 SNIP 1.128
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 1.389 SNIP 1.104
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 1.173 SNIP 1.007
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 1.093 SNIP 0.925
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 1.122 SNIP 0.973
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 1.09 SNIP 0.914
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 0.948 SNIP 1.068
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 0.121 SNIP 0
Gold Mining by Alkanethiol Radicals: Vacancies and Pits in the Self-Assembled Monolayers of 1-Propanethiol and 1-Butanethiol on Au(111)

Scanning-tunneling microscopy (STM) under electrochemical control (in situ STM) in aqueous solution, combined with a priori density functional theory (DFT) image simulations at room temperature, reveals the atomic nature of the interface between Au(111) and self-assembled monolayers (SAMs) of 1-propanethiol and 1-butanethiol. Use of single-crystal gold substrates allows for both high-resolution images of the surface cell internal structure and the evaluation of pit densities on large surface terraces, while room-temperature STM image simulations facilitate discrimination between possible atomic interface structures. For both adsorbates, the high-coverage c(4 × 2) phase is identified as (3 × 2√3)-4, while the medium-coverage striped phase of 1-propanethiol SAMs is identified as (7 × √3)-4. All of these structures contain two adatom-bound adsorbates of the form RS–Au–SR (R = CnH2n+1S•) per surface unit cell. The observed pit coverages of 2.8–4.0% are much less than those typically found for methanethiol SAMs (ca. 12–20%), indicating that one of the two gold adatoms per cell in 1-propanethiol and 1-butanethiol SAMs is extracted to form a local surface vacancy rather than a coalesced surface pit. The surface vacancy appears free to diffuse within each cell on the STM time scale, with only small STM image changes associated with vacancy localization. Significantly, the c(4 × 2) phases of 1-propanethiol and 1-butanethiol SAMs give quite different STM images. 1-Butanethiol SAMs show characteristics similar to those of longer linear alkanethiols with four bright spots per cell, while the 1-propanethiol SAM displays five bright spots organized in a different pattern. These differences are rationalized by a more uniform vacancy distribution and rigid structure for 1-butanethiol SAMs, compared to the different diffusionally labile vacancy configurations and higher lateral S–C–C–C conformational flexibility found for 1-propanethiol. Also, the differences in interface structure from that of methanethiol SAMs are rationalized in terms of varying pit coalescence energies. These subtle differences underline the striking diversity in the electronic and molecular structural packing even within a single class of closely related molecular adsorbates.

General information
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Organisations: NanoChemistry, Department of Chemistry, University of Sydney
Authors: Wang, Y. (Ekstern), Chi, Q. (Intern), Hush, N. S. (Ekstern), Reimers, J. R. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
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Main Research Area: Technical/natural sciences

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Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.917 SNIP 1.268 CiteScore 4.68
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 2.027 SNIP 1.448 CiteScore 5.08
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BFI (2013): BFI-level 1
Scopus rating (2013): SJR 2.134 SNIP 1.439 CiteScore 5.14
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
Investigation of Streptococcus mutans biofilm growth on modified Au(111)-surfaces using AFM and electrochemistry

Biofilms of the bacterium Streptococcus mutans constitute perhaps the most important direct cause of human dental caries formation. We have studied S. mutans biofilm formation and properties on Au(111)-surfaces modified by self-
assembled molecular monolayers (SAMs) of different thiol-based molecules based on a combination of atomic force microscopy (AFM) and electrochemistry using single-crystal Au(111)-surfaces. The thiols include both small, strongly hydrophilic molecules (cysteamine and the amino acid L-Cystein) and long straight-chain alkanethiol-based molecules with either hydrophobic (hexadecanethiol, MHD) or hydrophilic (mercapto-hexadecanoic acid, MHDA) end groups. The voltammetric reductive desorption (RD) peaks of the thiol-based SAMs in the absence and presence of biofilms and growth medium was in focus as a sensitive probe of the SAM local environment. AFM showed that S. mutans had grown to dense monolayers on all the four modified Au(111)-surfaces after 24 hour. The growth rates were slightly different and fastest for MHD-modified surfaces but the biofilms after 24 hour were indistinguishable. Reductive desorption signals of all the four compounds in phosphate buffer, pH 7.4 were very similar in the absence and presence of the biofilms and growth medium. RD in strongly alkaline solution where RD peak resolution is higher was also addressed. Most notably, the strong RD peaks of the long pure and functionalized MHD and MHDA in 0.1M NaOH remained in the presence either of biofilm together with growth medium or of the growth medium alone. The RD peak potential of the hydrophilic MHDA surface remained, further largely unaffected but the RD peak of the hydrophobic MHD SAM is distinctly shifted compared to the MHD SAM alone. The shifts were further in different directions for the S. mutans biofilm plus growth medium (negative shift) and for the growth medium alone (positive shift). Both the AFM images and the electrochemical data suggest that the biofilms form more efficiently and interact more strongly with the hydrophobic surface than with the hydrophilic surfaces.

**General information**

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Organisations: NanoChemistry, Department of Chemistry  
Authors: Hu, Y. (Intern), Zhang, J. (Intern), Ulstrup, J. (Intern)  
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BFI (2018): BFI-level 1  
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Web of Science (2017): Indexed Yes  
BFI (2016): BFI-level 1  
Scopus rating (2016): SJR 0.741 SNIP 0.844 CiteScore 2.97  
Web of Science (2016): Indexed yes  
BFI (2015): BFI-level 1  
Scopus rating (2015): SNIP 0.88 SJR 0.723 CiteScore 2.73  
BFI (2014): BFI-level 1  
Scopus rating (2014): SNIP 0.954 SJR 0.835 CiteScore 2.81  
BFI (2013): BFI-level 2  
Scopus rating (2013): SJR 1.099 SJR 0.912 CiteScore 2.92  
ISI indexed (2013): ISI indexed yes  
BFI (2012): BFI-level 2  
Scopus rating (2012): SJR 1.023 SJR 1.081 CiteScore 2.72  
ISI indexed (2012): ISI indexed yes  
BFI (2011): BFI-level 2  
Scopus rating (2011): SJR 1.125 SJR 1.066 CiteScore 2.89  
ISI indexed (2011): ISI indexed yes  
Web of Science (2011): Indexed yes  
BFI (2010): BFI-level 2  
Scopus rating (2010): SJR 1.108 SJR 1.157  
BFI (2009): BFI-level 2  
Scopus rating (2009): SJR 1.12 SJR 1.012  
BFI (2008): BFI-level 2  
Scopus rating (2008): SJR 1.135 SJR 1.26  
Web of Science (2008): Indexed yes
Saccharide-based Approach to Green Metallic Nanostructure Synthesis
A green approach to solution synthesis of metallic nanoparticles has been developed using harmless and bioapplicable chemicals as well as moderate temperatures. Metal precursors are reduced by glucose/buffers and sterically stabilized by starch. The saccharide based procedure is highly diverse producing specifically a wide range of spherical, anisotropic, metallic, semi-conductor and core-shell nanostructures.

General information
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Organisations: Department of Chemistry, NanoChemistry, Technical University of Denmark
Authors: Engelbrekt, C. (Intern), Sørensen, K. H. (Ekstern), Jensen, P. S. (Intern), Ulstrup, J. (Intern), Zhang, J. (Intern)
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Main Research Area: Technical/natural sciences
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Single-molecule Bioelectrochemistry

General information
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Organisations: Department of Chemistry, NanoChemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Ulstrup, J. (Intern)
Publication date: 2011
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Single-molecule conductivity of non-redox and redox molecules at pure and gold-mined Au(111)-electrode surfaces
The structure, two-dimensional organization, and function of molecules immobilized on solid surfaces can be addressed in a degree of detail that has reached the level of the single-molecule. In this context redox molecules are “smart” molecules adding sophisticated electronic function. Redox metalloproteins such as blue copper, heme, and iron-sulfur proteins as
well as redox metalloenzymes are other new targets for single-molecule electrochemical and bioelectrochemical surface science. Electrochemistry combined with scanning tunneling and atomic force microscopy in aqueous chemical or biological media supported by comprehensive theoretical frames, have emerged as core approaches in these exciting areas. Single-molecule redox electrochemistry is rooted in two major areas. One is the preparation of well-defined (atomically planar) electrode surfaces modified by molecular monolayers (SAMs). High-resolution in situ STM combined with large-scale theoretical computations have offered detailed insight in the surface binding modes of functionalized alkanethiols on Au-surfaces in particular. Such surfaces have disclosed a variety of surface structures that involve both direct binding to a planar Au and binding to surface-mined Au-atoms. In addition the SAMs ensure protein/enzyme immobilization gentle enough that the proteins retain electron transfer or enzyme activity in a variety of local environments. The second area is the mapping and control of the immobilized redox molecules and metalloproteins themselves. Single-molecule resolution has also here been achieved, both in structural mapping and in controlled single-molecule electron transport and enzyme function on SAM surfaces such as those now characterized to (sub)-molecular resolution.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, University of Sydney
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Ulstrup, J. (Intern), Wang, Y. (Ekstern), Hush, N. S. (Ekstern), Reimers, J. R. (Ekstern)
Publication date: 2011
Main Research Area: Technical/natural sciences
Electronic versions:
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Bibliographical note
Invited talk
Source: orbit
Source-ID: 316383
Publication: Research - peer-review › Conference abstract for conference – Annual report year: 2011

Insulins struktur og kemiske egenskaber i nanoskala og på det enkelte molekyles niveau

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry
Authors: Welinder, A. C. (Intern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Publication date: Jun 2010

Publication information
Place of publication: Kgs. Lyngby, Denmark
Publisher: Technical University of Denmark (DTU)
Original language: English
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 271217
Publication: Research › Ph.D. thesis – Annual report year: 2010

1.7 nm Platinum Nanoparticles: Synthesis with Glucose Starch, Characterization and Catalysis
Monodisperse platinum nanoparticles (PtNPs) were synthesized by a green recipe. Glucose serves as a reducing agent and starch as a stabilization agent to protect the freshly formed PtNP cores in buffered aqueous solutions. Among the ten buffers studied, 2-(N-morpholino)ethanesulfonic acid (MES), ammonium acetate and phosphate are the best media for PtNP size control and fast chemical preparation. The uniform sizes of the metal cores were determined by transmission electron microscopy (TEM) and found to be 1.8 +/- 0.5, 1.7 +/- 0.2 and 1.6 +/- 0.5 nm in phosphate, MES and ammonium acetate buffer, respectively. The estimated total diameter of the core with a starch coating layer is 5.8-6.0 nm, based on thermogravimetric analysis (TGA). The synthesis reaction is simple, environmentally friendly, highly reproducible, and easy to scale up. The PtNPs were characterized electrochemically and show high catalytic activity for reduction of dioxygen and hydrogen peroxide as well as for oxidation of dihydrogen. The PtNPs can be transferred to carbon support materials with little demand for high specific surface area of carbon. This enables utilization of graphitized carbon blacks to prepare well-dispersed Pt/C catalysts, which exhibit significantly improved durability in the accelerated aging test under fuel cell mimicking conditions.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Energy and Materials
Authors: Engelbrekt, C. (Intern), Sørensen, K. H. (Ekstern), Lubcke, T. (Ekstern), Zhang, J. (Intern), Li, Q. (Intern), Pan, C. (Intern), Bjerrum, N. (Intern), Ulstrup, J. (Intern)
Adsorption of human insulin on single-crystal gold surfaces investigated by in situ scanning tunnelling microscopy and electrochemistry

We have explored the adsorption of zinc-free human insulin on the three low-index single-crystalline Au(111)-, Au(100)- and Au(110)-surfaces in aqueous buffer (KH2PO4, pH 5) by a combination of electrochemical scanning tunnelling microscopy (in situ STM) at single-molecule resolution and linear sweep, LSV, cyclic, CV, and square wave (SQWV) voltammetry. Multifarious electrochemical patterns were observed. Most attention was given to reductive desorption caused by insulin binding to the Au-surfaces via up to three disulfide groups per insulin monomer, presumably converted to single Au-S links. SQWV suggested the Au-S bond strength order Au(111) > Au(110) > Au(100) based on the reductive desorption potentials. The voltammetric diversity was paralleled by different in situ STM insulin adsorption modes on the three surfaces. Single-molecule resolution was achieved in all cases. The coverage followed the order Au(110) > Au(100) > Au(111) and differs from the reductive desorption order that records the Au-S bonding element. Evenly distributed single molecules were scattered over large Au(111)-terraces, with intriguing molecular arrays disclosed near the terrace edges.

In comparison, high-density molecular scale structures were observed both over the terraces and across terrace edges on Au(100). Larger rectangular structures also appeared (8-12% coverage). These are Au-islands from the lift of the reconstruction. Notably, 10 x 10 nm(2) patches of highly ordered much smaller structures, possibly from insulin decomposition emerged sporadically within the dense insulin adlayer. Insulin adsorbed in highest coverage on the Au(110) and followed the directional surface topology with insulin molecules aligned in the Au(110)-surface grooves, occasionally "spilling over" and merging into larger structures. Adsorption, Au-S binding, and insulin unfolding are all parts of insulin surface behaviour and reflected in both voltammetry and in situ STM. In spite of these complications, the data show that molecular scale resolution has been achieved and offer other perspectives of insulin surface science such as single-molecule mapping of the insulin monomer/dimer-hexamer interconversion.
Approach to Interfacial and Intramolecular Electron Transfer of the Diheme Protein Cytochrome c(4) Assembled on Au(111) Surfaces

Intramolecular electron transfer (ET) between metal centers is a core feature of large protein complexes in photosynthesis, respiration, and redox enzyme catalysis. The number of microscopic redox potentials and ET rate constants is, however, prohibitive for experimental cooperative ET mapping, but two-center proteins are simple enough to offer complete communication networks. At the same time, multicenter redox proteins operate in membrane environments where conformational dynamics may lead to gated ET features different from conditions in homogeneous solution. The bacterial respiratory diheme protein Pseudomonas stutzeri cytochrome c(4) has been a target for intramolecular, interheme ET. We report here voltammetric and in situ scanning tunneling microscopy (STM) data for P. stutzeri cyt c(4) at single-crystal, atomically planar Au(111)-electrode surfaces modified by variable-length omega-mercapto-alkanoic carboxylic acids. As evidenced by in situ STM, the strongly dipolar protein is immobilized in a close to vertical orientation at this surface with the positively charged high-potential heme domain adjacent to the electrode. This orientation gives asymmetric voltammograms with two one-ET peaks in the cathodic direction and a single two-ET peak in the anodic direction. Intramolecular, interheme ET with high, 8,000-30,000 s(-1), rate constants is notably an essential part of this mechanism. The high rate constants are in striking contrast to ET reactions of P. stutzeri cyt c4 with small reaction partners in homogeneous solution for which kinetic analysis clearly testifies to electrostatic cooperative effects but no intramolecular,
interheme ET higher than 0.1-10 s(-1). This difference suggests a strong gating feature of the process. On the basis of the three-dimensional structure of P. stutzeri cyt c(4), gating is understandable due to the through-space, hydrogen-bonded electronic contact between the heme propionates which is highly sensitive to environmental configurational fluctuations.

**General information**

State: Published
Organisations: NanoChemistry, Department of Chemistry, Metalloprotein Chemistry and Engineering
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Taner, A. (Intern), Borg, L. (Intern), Pedersen, G. W. (Ekstern), Christensen, H. E. M. (Intern), Nazmudtinov, R. R. (Ekstern), Ulstrup, J. (Intern)
Pages: 5617-5624
Publication date: 2010
Main Research Area: Technical/natural sciences

**Publication information**

Journal: Journal of Physical Chemistry Part B: Condensed Matter, Materials, Surfaces, Interfaces & Biophysical
Volume: 114
Issue number: 16
ISSN (Print): 1520-6106
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 3.03 SJR 1.348 SNIP 1.02
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.367 SNIP 1.096 CiteScore 3.25
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.44 SNIP 1.14 CiteScore 3.28
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.494 SNIP 1.2 CiteScore 3.53
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.92 SNIP 1.251 CiteScore 3.66
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.78 SNIP 1.226 CiteScore 3.62
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.849 SNIP 1.214
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 2.232 SNIP 1.349
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 2.543 SNIP 1.381
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.346 SNIP 1.282
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.369 SNIP 1.415
Web of Science (2006): Indexed yes
We have studied Streptococcus mutans (S. mutans) biofilm growth and growth inhibition on Au(111)-surfaces using atomic force microscopy (AFM) and interfacial electrochemistry of a number of redox probe molecules. AFM of the biofilm growth and growth inhibition on both mica and Au(111)-surfaces was followed by sampling at given times, drying the samples naturally, and imaging. The electrochemical investigations were based on single-crystal Au(111)-electrode surfaces to exclude polycrystallinity as a cause of inhomogeneous voltammetric broadening on the biofilm covered electrode surfaces. The redox couples were chosen for their positive ([Ru(NH₃)(6)]²⁺⁻, [Co(terpy)(2)]²⁺⁻, terpy = 2,2',2''-terpyridine) or negative ([Fe(CN)(6)]⁻⁻, [IrCl₆](3-)⁻⁻) electrostatic charge, [Co(NH₃)(6)]²⁺⁻ and [Co(phen)(3)]²⁺⁻ (phen = 1,10-phenanthroline) were other inhibition factors investigated. The positively and negatively charged redox probe couples displayed antagonistic inhibition and voltammetric patterns. [Ru(NH₃)(6)]²⁺⁻ and the homologous compound [Co(NH₃)(6)]²⁺⁻ were the only probe compounds to effect growth inhibition. On the other hand, cyclic voltammetry (CV) of both [Ru(NH₃)(6)]²⁺⁻ (positively charged, biofilm growth inhibitor) and [Co(terpy)(2)]²⁺⁻ (positively charged, no biofilm growth inhibition) displayed fully reversible CV on biofilm covered electrodes, almost indistinguishable from CV at bare Au(111)-electrode surfaces. In comparison, CVs of [Fe(CN)(6)]⁻⁻ and [IrCl₆](3-)⁻⁻ (both negatively charged and no growth inhibition) were distorted from planar diffusion behavior on bare Au(111)-electrode surfaces toward spherical diffusion behavior on S. mutans biofilm covered Au(111)-electrode surfaces. DNAase treatment of the biofilm covered Au(111)-electrode surface partly restores planar diffusion CV of [Fe(CN)(6)]⁻⁻ and [IrCl₆](3-)⁻⁻-. This is reflected in a decrease of the growth rate and the appearance of molecular-scale structures near the bacterial edges as imaged by AFM after DNAase treatment. A rationale for the different voltammetric behavior of positively and negatively charged redox probe molecules based on electrostatic properties of the local surface environment is offered.
Green Platinum Nanoparticles: Synthesis, Characterization and Function

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Department of Energy Conversion and Storage, Proton conductors, Technical University of Denmark
Authors: Engelbrekt, C. (Intern), Sørensen, K. H. (Ekstern), Lübcke, T. (Ekstern), Zhang, J. (Intern), Li, Q. (Intern), Pan, C. (Intern), Bjerrum, N. (Intern), Ulstrup, J. (Intern)
Publication date: 2009
Main Research Area: Technical/natural sciences
Electronic versions:
Poster_for_NanoDay_Dec_7th_2009.jpg
Source: PublicationPreSubmission
Source-ID: 101972358
Publication: Research - peer-review › Poster – Annual report year: 2009

Green Synthesis of Gold nanoparticles with Starch-glucose and Application in Bioelectrochemistry
A method for gold nanoparticle (AuNP) synthesis from buffered glucose and starch solution has been developed and the particles investigated by UV-Vis spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM) and electrochemistry. The synthesis proceeds smoothly in neutral and basic solution. The starch concentration, temperature and chemical nature of the buffers are key factors in the AuNP formation. Glucose and starch are reducing and protecting agents, respectively. Among several inorganic and biological Good's buffers, phosphate and MES buffers give the best results with quite uniform AuNPs. Other buffers do not result in well-defined nanoparticle structures. Typical AuNP diameters from MES and phosphate buffers (PB) are 4 ± 1 nm and 13 ± 2 nm with plasmon band peaks at 521 nm and 523 nm, respectively. The role of the phosphate buffer is mainly to control the pH, while MES is also a synergist with more composite function. AuNPs prepared by this method are stable in solution even after 17 months at room temperature. TEM confirms the crystalline structure of the AuNPs, meaning that the AuNP surfaces are low-index single-crystal facets such as (100), (110) and (111). Electrochemistry of the buffers at such single-crystal gold electrode surfaces has offered a more detailed understanding of the buffer effect. The AuNPs have been successfully used in bioelectrochemistry, and found to efficiently enhance interfacial electrochemical electron transfer of the metalloprotein yeast cytochrome c in homogeneous solution. The synthesis has been extended successfully to direct use of starch-rich foods such as potato, carrot and onion to synthesize AuNPs. The present work thus offers a gentle and non-toxic procedure for the synthesis of monodisperse AuNPs in neutral medium with promising potential for pH sensitive biological or medically related applications.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Technical University of Denmark
Authors: Engelbrekt, C. (Intern), Sørensen, K. H. (Ekstern), Zhang, J. (Intern), Welinder, A. C. (Intern), Jensen, P. S. (Intern), Ulstrup, J. (Intern)
Pages: 7839-7847
Publication date: 2009
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Materials Chemistry
Volume: 19
Issue number: 42
ISSN (Print): 0959-9428
Ratings:
BFI (2015): BFI-level 2
BFI (2014): BFI-level 2
BFI (2013): BFI-level 2
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 2
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Long-Range Interfacial Electrochemical Electron Transfer of Pseudomonas aeruginosa Azurin-Gold Nanoparticle Hybrid Systems

We have prepared a "hybrid" of the blue copper protein azurin (Pseudomonas aeruginosa) and a 3 nm gold nanoparticle (AuNP). The AuNP/azurin hybrid was assembled on a Au(111)-electrode surface in a two-step process. The AuNP was first attached to the Au(111) electrode via Au-S chemisorption of a 4,4'-biphenyldithiol (4,4'-BPDT) monolayer. This was followed by 1-decanethiol modification of the bound AuNP and hydrophobic binding of azurin to the AuNP. The Au(111)/AuNP/azurin system was characterized by atomic force microscopy (AFM), cyclic voltammetry (CV), and in situ electrochemical scanning tunneling microscopy (in situ STM). AFM and STM point to the feasibility of preparing both dense and sparsely populated AuNP monolayers. CV shows two pairs of voltammetric peaks at high scan rates, both around the azurin equilibrium potential. One pair of redox peaks follows closely that of azurin hydrophobically immobilized directly on a Au(111)/1-tetradecanethiol reference surface. The other pair, tentatively assigned to the AuNP/azurin hybrid, shows a 20-fold electron transfer rate enhancement over the reference system. This dual pattern is supported by in situ STM which shows two distinct contrasts. A strong contrast most likely arises either from azurin-free AuNPs or from AuNP-free azurin displaced onto the Au(111)/4,4'-BPDT surface. The other contrast, assigned to the AuNP/azurin hybrid, is weaker and fluctuates in time. Mechanisms of electronic conductivity of the AuNP/azurin system are discussed.

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry
Authors: Jensen, P. S. (Intern), Chi, Q. (Intern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Pages: 13993-14000
Publication date: 2009
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Physical Chemistry Part C: Nanomaterials and Interfaces
Volume: 113
Issue number: 31
ISSN (Print): 1932-7447
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 4.48 SJR 1.948 SNIP 1.181
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.917 SNIP 1.268 CiteScore 4.68
Metallic Nanostructures: Synthesis, Characterization and Function

General information

State: Published
Organisations: Department of Chemistry, NanoChemistry, Technical University of Denmark
Authors: Engelbrekt, C. (Intern), Sørensen, K. H. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Main Research Area: Technical/natural sciences

Electronic versions:

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Source: PublicationPreSubmission
Source-ID: 101972352
Publication: Research - peer-review › Poster – Annual report year: 2009
Organic compounds inhibiting S. epidermidis adhesion and biofilm formation

The formation of biofilms on surfaces of indwelling medical devices is a serious medical problem. Staphylococcus epidermidis is a common pathogen found to colonize implanted devices and as a biofilm is more resistant to the host immune system as well as to antibiotic treatments. Combating S. epidermidis infections by preventing or eradicating biofilm formation of the bacterium is therefore a medically important challenge. We report here a study of biofilm formation of S. epidermidis on solid surfaces using a combination of confocal laser scanning (CLSM) and atomic force microscopy (AFM) in both air and aqueous environments. We have investigated the inhibitory effects of surfaces treated with four organic compounds, two benzoate derivatives denoted as compound 59 and 75 and two carboxamide derivatives denoted as compound 47 and 73, on S. epidermidis adhesion and biofilm formation. All four compounds evoke significant inhibitory effects on the formation of S. epidermidis biofilms with compounds 47 and 73 being most effective. None of the compounds were found to inhibit growth of S. epidermidis in liquid cultures. Bacteria attached to the substrate when exposed to the compounds were not affected indicating that these compounds inhibit initial adhesion. These results suggest a pretreatment for medically implanted surfaces that can prevent the biofilm formation and reduce infection.

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Department of Systems Biology, Center for Systems Microbiology
Authors: Qin, Z. (Ekstern), Zhang, J. (Intern), Hu, Y. (Intern), Chi, Q. (Intern), Mortensen, N. P. (Intern), Qu, D. (Ekstern), Molin, S. (Intern), Ulstrup, J. (Intern)
Pages: 881-888
Publication date: 2009
Conference: International Scanning Probe Microscopy Conference, Seattle, WA, 01/01/2008
Main Research Area: Technical/natural sciences

Publication information
Journal: Ultramicroscopy
Volume: 109
Issue number: 8
ISSN (Print): 0304-3991
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.82 SJR 1.915 SNIP 1.233
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 2.121 SNIP 1.428 CiteScore 2.78
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.638 SNIP 1.661 CiteScore 2.59
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.777 SNIP 1.337 CiteScore 2.66
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.867 SNIP 1.595 CiteScore 2.31
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.624 SNIP 1.338 CiteScore 2.35
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.712 SNIP 1.236
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Self-assembled monolayers (SAMs) formed by chemisorption of a branched-chain alkanethiol, 2-methyl-1-propanethiol, on Au(111) surfaces were studied by in situ scanning tunneling microscopy (STM) under electrochemical potential control and analyzed using extensive density functional theory (DFT) calculations. The SAM forms in the unusual \((8 \times \sqrt{3})-4\) superlattice, producing a very complex STM image. Seventy possible structures were considered for the SAM, with the calculated lowest-energy configuration in fact predicting the details of the unusual observed STM image. The most stable structure involves two \(R-S-Au-S-R\) adatom-mediated motifs per surface cell, with steric-induced variations in the adsorbate alignment inducing the observed STM image contrasts. Observed pits covering \(5.6 \pm 0.5\%\) of the SAM surface are consistent with this structure. These results provide the missing link from the structural motifs observed on surfaces at low coverage and on gold nanoparticles to the observed spectroscopic properties of high-coverage SAMs formed by methanethiol. However, the significant role attributed to intermolecular steric packing effects suggests a lack of generality for the adatom-mediated motif at high coverage.

**General information**

State: Published
Organisations: NanoChemistry, Department of Chemistry, Center for Nanoteknologi, University of Sydney
Authors: Wang, Y. (Ekstern), Chi, Q. (Intern), Hush, N. S. (Ekstern), Reimers, J. R. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Pages: 19601-19608
Publication date: 2009
Main Research Area: Technical/natural sciences

**Publication information**

Journal: Journal of Physical Chemistry Part C: Nanomaterials and Interfaces
Volume: 113
Issue number: 45
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BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
Structural Mapping and Interfacial Electron Transfer towards the Single-molecule Level, invited keynote talk

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Jensen, P. S. (Intern), Hansen, A. G. (Intern), Welinder, A. C. (Intern), Ulstrup, J. (Intern)
Publication date: 2009
Submolecular Electronic Mapping of Single Cysteine Molecules by In Situ Scanning Tunneling Imaging

We have used L-Cysteine (Cys) as a model system to study the surface electronic structures of single molecules at the submolecular level in aqueous buffer solution by a combination of electrochemical scanning tunneling microscopy (in situ STM), electrochemistry including voltammetry and chronocoulometry, and density functional theory (DFT) computations. Cys molecules were assembled on single-crystal Au(110) surfaces to form a highly ordered monolayer with a periodic lattice structure of c(2 x 2) in which each unit contains two molecules; this conclusion is confirmed by the results of calculations based on a slab model for the metal surface. The ordered monolayer offers a platform for submolecular scale electronic mapping that is an issue of fundamental interest but remains a challenge in STM imaging science and surface chemistry. Single Cys molecules were mapped as three electronic subunits contributed mainly from three chemical moieties: thiol (-SH), carboxylic (-COOH), and amine (-NH2) groups. The contrasts of the three subunits depend on the environment (e.g., pH), which affects the electronic structure of adsorbed species. From the DFT computations focused on single molecules, rational analysis of the electronic structures is achieved to delineate the main factors that determine electronic contrasts in the STM images. These factors include the molecular orientation, the chemical nature of the elements or groups in the molecule, and the interaction of the elements with the substrate and tip. The computational images recast as constant-current-height profiles show that the most favorable molecular orientation is the adsorption of cysteine as a radical in zwitterionic form located on the bridge between the Au(I 10) atomic rows and with the amine and carboxyl group toward the solution bulk. The correlation between physical location and electronic contrast of the adsorbed molecules was also revealed by the computational data. The present study shows that cysteine packing in the adlayer on Au(110) from the liquid environment is in contrast to that from the ultrahigh-vacuum environment, suggesting solvent plays a role during molecular assembly.
Charge transfer and Interfacial bioelectrochemistry at the nanoscale and single-molecule levels

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Russian Academy of Sciences
Authors: Zhang, J. (Intern), Albrecht, T. (Intern), Chi, Q. (Intern), Kuznetsov, A. M. (Ekstern), Ulstrup, J. (Intern)
Pages: 251-304
Publication date: 2008

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Title of host publication: Bioinorganic Electrochemistry
Place of publication: Guilford, UK
Publisher: Springer
Editors: Hammerich, O., Ulstrup, J.
ISBN (Print): 1402064993
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 257720
Hydrogen Evolution on Supported Incomplete Cubane-type \([\text{Mo3S4}(4^+)\] Electrocatalsys

Electrocatalytic properties of biomimetic supported incomplete cubane-type \([\text{Mo3S4}(4^+)\] clusters are investigated. The activity toward the hydrogen evolution reaction (HER) is evaluated on both a high surface area gas diffusion electrode in a membrane electrode assembly and on highly orientated pyrolytic graphite (HOPG) supports. Sub-monolayers of the clusters were imaged by means of scanning tunnelling microscopy (STM) prior to electrochemical characterization. This enabled the quantification of the activity on a per cluster basis for the HER and the comparison of the activity with other HER catalysts. We find that the HER activity of the \([\text{Mo3S4}(4^+)\] is comparable with that of the edge sites of MoS2. The supported \([\text{Mo3S4}(4^+)\] molecules were also characterized by X-ray photoelectron spectroscopy (XPS), and the observed deterioration in electrocatalytic activity with time was assigned to slow \([\text{Mo3S4}(4^+)\] cathodic desorption from the catalyst support.

General information
State: Published
Organisations: Department of Physics, NanoChemistry, Department of Chemistry, Metalloprotein Chemistry and Engineering, Experimental Surface and Nanomaterials Physics, Center for Individual Nanoparticle Functionality, Center for Nanoteknologi
Authors: Jaramillo, T. (Intern), Bonde, J. L. (Intern), Zhang, J. (Intern), Ooi, B. L. (Intern), Andersson, K. J. (Intern), Ulstrup, J. (Intern), Chorkendorff, I. (Intern)
Pages: 17492-17498
Publication date: 2008
Main Research Area: Technical/natural sciences

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Journal: Journal of Physical Chemistry C
Volume: 112
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Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 4.48 SJR 1.948 SNIP 1.181
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.917 SNIP 1.268 CiteScore 4.68
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 2.027 SNIP 1.448 CiteScore 5.08
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 2.134 SNIP 1.439 CiteScore 5.14
Single-molecule Electron Transfer in Electrochemical Environments

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, A. N. Frumkin Institute of Electrochemistry, Imperial College London
Authors: Zhang, J. (Intern), Kuznetsov, A. (Ekstern), Medvedev, I. (Ekstern), Chi, Q. (Intern), Jensen, P. S. (Intern), Albrecht, T. (Ekstern), Ulstrup, J. (Intern)
Pages: 2737-2791
Publication date: 2008
Main Research Area: Technical/natural sciences

Publication information
Journal: Chemical Reviews
Volume: 108
Issue number: 7
ISSN (Print): 0009-2665
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Surface-induced intramolecular electron transfer in multi-centre redox metalloproteins: The di-haem protein cytochrome c4 in homogeneous solution and at electrochemical surfaces

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Kazan State Technological University
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Jensen, P. S. (Intern), Nasmudtinov, R. (Ekstern), Ulstrup, J. (Intern)
Pages: 7
Publication date: 2008
Main Research Area: Technical/natural sciences

Publication information
Chemisorbed and physisorbed structures for 1,10-phenanthroline and dipyrido[3,2-a:2',3'-c]phenazine on Au(111)

Scanning tunneling microscopy (STM) images of 1,10-phenanthroline (PHEN) and dipyrido[3,2-a:2',3'-c]phenazine (DPPZ) on Au(111) are recorded using both in situ and ex situ techniques. The images of PHEN depict regimes of physisorption and chemisorption, whereas DPPZ is only physisorbed. All physisorbed structures are not pitted and fluctuate dynamically, involving aligned (4 x 4) surface domains with short-range (ca. 20 molecules) order for PHEN but unaligned chains with medium-range (ca. 100 molecules) order for DPPZ. In contrast, the chemisorbed PHEN monolayers remain stable for days, are associated with surface pitting, and form a (4 x root 13)R46 degrees lattice with long-range order. The density of pitted atoms on large gold terraces is shown to match the density of chemisorbed molecules, suggesting that gold adatoms link PHEN to the surface. For PHEN, chemisorbed and physisorbed adsorbate structures are optimized using plane-wave density-functional theory (DFT) calculations for the surface structure. Realistic binding energies are then obtained adding dispersive corrections determined using complete-active-space self-consistent-field calculations using second-order perturbation theory (CASPT2) applied to cluster-interaction models. A fine balance between the large adsorbate-adsorbate dispersive forces, adsorbate-surface dispersive forces, gold ligation energy, and surface mining energy is shown to dictate the observed phenomena, leading to high surface mobility and substrate/surface lattice incommensurability. Increasing the magnitude of the dispersive forces through use of DPPZ, rather than PHEN, to disturb this balance produced physisorbed monolayers without pits and/or surface registration but with much longer-range order. Analogies are drawn with similar but poorly understood processes involved in the binding of thiols to Au(111).
Kinetics and mechanism of the acid transition of the active site in plastocyanin

General information
State: Published
Organisations: Metalloprotein Chemistry and Engineering, Department of Chemistry, NanoChemistry, University of Copenhagen
Authors: Hass, M. A. S. (Ekstern), Christensen, H. E. M. (Intern), Zhang, J. (Intern), Led, J. J. (Ekstern)
Pages: 14619-14628
Publication date: 2007
Main Research Area: Technical/natural sciences

Publication information
Journal: Biochemistry
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BFI (2018): BFI-level 1
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BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.8
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): CiteScore 3.02
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scanning tunneling microscopy under full electrochemical potential control (in situ STM) has been used extensively as an efficient method to characterize microstructures at solid/liquid interfaces at the atomic and molecular levels. However, under ambient conditions oxygen may interfere in open in situ STM systems by diffusion through the solutions. Such interference can be serious for oxygen sensitive systems both for the target molecules themselves and for chemical linker molecules bound to the electrode surface for example, via Au-S bonding. This is strikingly illustrated in the present report. We present here oxygen-free in situ STM, in which the samples are contained in an argon atmosphere which removes oxygen in the system. Interference from oxygen is profoundly reduced in this setup and demonstrated by three examples. Two of these are in situ STM of the intermediate-size sulfur containing organic molecule cysteamine and the biomolecule homocysteine. The third example is the iron-sulfur protein ferredoxin (Pyrococcus furiosus). Monolayers of these molecules on Au(111) are imaged to molecular resolution and the images compared in the presence and absence of oxygen. In all the cases, the STM image quality of the monolayer structures has improved significantly in the absence of oxygen. Reasons for the drastic effects of dioxygen based on both chemical surface reactivity and electron scattering effects are discussed. These observations are important in general for STM of oxygen sensitive chemical and biological samples.

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry
Authors: Zhang, J. (Intern), Ulstrup, J. (Intern)
Pages: 213-220
Publication date: 2007
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Electroanalytical Chemistry
Single-molecule conductance of redox molecules in electrochemical scanning tunneling microscopy

Experimental data and theoretical notions are presented for 6-[1'-(6-mercapto-hexyl)-[4,4']bipyridinium]-hexane-1-thiol iodide (6V6) "wired" between a gold electrode surface and tip in an in situ scanning tunneling microscopy configuration.
The viologen group can be used to "gate" charge transport across the molecular bridge through control of the electrochemical potential and consequently the redox state of the viologen moiety. This gating is theoretically considered within the framework of superexchange and coherent two-step notions for charge transport. It is shown here that the absence of a maximum in the I-tunneling versus electrode potential relationship can be fitted by a "soft" gating concept. This arises from large configurational fluctuations of the molecular bridge linked to the gold contacts by flexible chains. This view is incorporated in a formalism that is well-suited for data analysis and reproduces in all important respects the 6V6 data for physically sound values of the appropriate parameters. This study demonstrates that fluctuations of isolated configurationally "soft" molecules can dominate charge transport patterns and that theoretical frameworks for compact monolayers may not be directly applied under such circumstances.
Voltammetry and electrocatalysis of Achromobacter xylosoxidans copper nitrite reductase on functionalized Au(III)-electrode surfaces

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Metalloprotein Chemistry and Engineering, University of Copenhagen, Russian Academy of Sciences
Authors: Welinder, A. C. (Intern), Zhang, J. (Intern), Hansen, A. G. (Intern), Moth-Poulsen, K. (Ekstern), Christensen, H. E. M. (Intern), Kuznetsov, A. M. (Ekstern), Bjørnholm, T. (Ekstern), Ulstrup, J. (Intern)
Pages: 1343-1378
Publication date: 2007
Main Research Area: Technical/natural sciences

Publication information
Journal: Zeitschrift für Physikalische Chemie
Volume: 221
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Web of Science (2007): Indexed yes
Original language: English
DOI:
10.1524/zpch.2007.221.9-10.1343
Source-ID: 209486
Publication: Research - peer-review › Journal article – Annual report year: 2007

Adsorption and In Situ Scanning Tunneling Microscopy of Cysteine on Au(111): Structure, Energy and Tunneling Contrasts

General information
State: Published
Organisations: Department of Chemistry, Kazan Federal University
Authors: Nazmudtinov, R. (Ekstern), Zhang, J. (Intern), Zinkicheva, T. (Ekstern), Manyurov, I. (Ekstern), Ulstrup, J. (Intern)
Assembled Monolayers of Mo$_3$S$_4$$^+$ Clusters on Well-defined Surfaces

General information
State: Published
Organisations: Department of Chemistry, Department of Physics, Center for Individual Nanoparticle Functionality
Authors: Kristensen, J. (Ekstern), Zhang, J. (Intern), Chorkendorff, I. (Intern), Ulstrup, J. (Intern), Ooi, B. L. (Intern)
Pages: 3985-3990
Publication date: 2006
Main Research Area: Technical/natural sciences

Publication information
Journal: Dalton Transactions (Print Edition)
Volume: 33
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Ratings:
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Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.85 SJR 1.243 SNIP 0.931
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.351 SNIP 1.026 CiteScore 4.1
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.413 SNIP 1.085 CiteScore 4.06
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.436 SNIP 1.083 CiteScore 4.07
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.554 SNIP 1.001 CiteScore 3.79
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.505 SNIP 1.013 CiteScore 3.68
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.399 SNIP 0.875
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.928 SNIP 0.783
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Assembly Dynamics and Detailed Structure of 1-Propanethiol Monolayers on Au(111)-Surfaces Observed in Real Time by In Situ STM

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Ulstrup, J. (Intern)
Pages: 6203-6213
Publication date: 2006
Main Research Area: Technical/natural sciences

Publication information
Journal: Langmuir
Volume: 22
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Web of Science (2018): Indexed yes
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Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.99 SJR 1.55 SNIP 1.188
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.686 SNIP 1.308 CiteScore 4.33
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.816 SNIP 1.391 CiteScore 4.59
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 1.895 SNIP 1.356 CiteScore 4.55
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
Dynamics and Structure of the Formation of Cysteamine Monolayers on Au(111): Book of Abstracts p.120-121

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry
Authors: Zhang, J. (Intern), Ulstrup, J. (Intern)
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Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 194470
Publication: Research - peer-review › Journal article – Annual report year: 2006

Dynamics of Biomolecular Monolayers at Liquid-Solid Interfaces, invited keynote talk: Book of Abstracts p.86

General information
Electrocatalysis at Nanometer and Sub-Nanometer Scales: Hydrogen Evolution on Supported MoS2 and Mo3S4 Clusters

Kemi og Bioteknologi på Nanoskala og Enkeltmolekyle Niveau

Long-Range Interfacial Electron Transfer of Metalloproteins Based on Molecular Wiring Assemblies
Surface Microscopic Structure and Electrochemical Rectification of a Branched Alkanethiol Self-Assembled Monolayer

**General information**
State: Published
Organisations: Department of Chemistry
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Pages: 1102-1106
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Main Research Area: Technical/natural sciences

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Journal: Journal of Physical Chemistry B
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Publication: Research - peer-review › Letter – Annual report year: 2006

Voltammetry and In Situ Scanning Tunneling Microscopy of Cytochrome c Nitrite Reductase on Au(111)-Electrodes
Escherichia coli cytochrome c nitrite reductase (NrfA) catalyzes the six-electron reduction of nitrite to perform an important role in the biogeochemical cycling of nitrogen. Here we describe NrfA adsorption on single-crystal Au(111) electrodes as an electrocatalytically active film in which the enzyme undergoes direct electron exchange with the electrode. The adsorbed NrfA has been imaged to molecular resolution by in situ scanning tunneling microscopy (in situ STM) under full electrochemical potential control and under conditions where the enzyme is electrocatalytically active. Details of the density and orientational distribution of NrfA molecules are disclosed. The submonolayer coverage resolved by in situ STM is readily reconciled with the failure to detect nonturnover signals in cyclic voltammetry of the NrfA films. The molecular structures show a range of lateral dimensions. These are suggestive of a distribution of orientations that could account for the otherwise anomalously low turnover number calculated for the total population of adsorbed NrfA molecules when compared with that determined for solutions of NrfA. Thus, comparison of the voltammetric signals and in situ STM images offers a direct approach to correlate electrocatalytic and molecular properties of the protein layer, a long-standing issue in protein film voltammetry.

**General information**
State: Published
Organisations: Department of Chemistry, University of East Anglia
Authors: Gwyer, J. (Ekstern), Zhang, J. (Intern), Butt, J. (Ekstern), Ulstrup, J. (Intern)
Pages: 3897-3906
Publication date: 2006
Main Research Area: Technical/natural sciences

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- Web of Science (2017): Indexed Yes
- BFI (2016): BFI-level 1
- Scopus rating (2016): CiteScore 3.06 SJR 1.946 SNIP 1.018
- Web of Science (2016): Indexed yes
- BFI (2015): BFI-level 1
- Scopus rating (2015): SJR 2.145 SNIP 1.173 CiteScore 3.3
- Web of Science (2015): Indexed yes
- BFI (2014): BFI-level 1
- Scopus rating (2014): SJR 2.203 SNIP 1.166 CiteScore 3.33
- Web of Science (2014): Indexed yes
- BFI (2013): BFI-level 1
- Scopus rating (2013): SJR 2.229 SNIP 1.165 CiteScore 3.64
- ISI indexed (2013): ISI indexed yes
Coexistence of multiple conformations in cysteamine monolayers on Au(111)

The structural organization, catalytic function, and electronic properties of cysteamine monolayers on Au(111) have been addressed comprehensively by voltammetry, in situ scanning tunneling microscopy (STM) in anaerobic environment, and a priori molecular dynamics (MD) simulation and STM image simulation. Two sets of voltammetric signals are observed. One peak at -(0.65-0.70) V (SCE) is caused by reductive desorption of cysteamine. The other signal, at -(0.25-0.40) V consists of a peak doublet. The pH dependence of the latter suggests that the origin is catalytic dihydrogen evolution. The doublet feature is indicative of two distinct cysteamine configurations. Cysteamine monolayer formation from initial nucleation to a highly ordered phase has been successfully observed in real time using oxygen-free in situ STM. Random cellular patterns, disordered adlayer formation accompanied by high step edge mobility, and ultimately a highly ordered (root 3 x 4) R30 degrees lattice are observed sequentially. Pits are formed due to enclosure of the mobile edges during the adsorption process. In the highly ordered cysteamine layer, each unit has two spots with apparent 0.6 angstrom height difference in STM images. The coverage 5.7 +/- 0.1 x 10(-10) mol cm(-2) determined by voltammetry supports that the spots represent two individual cysteamine molecules. A priori MD and density functional simulations hold other clues to the image interpretation and indicate that the NH3+ groups dominate the tunneling contrast. A wide range of interface structures, showing variations in the sulfur binding site and orientation, gauche and trans conformers, and especially hydrogen-bonding interactions, are examined, from which it is concluded that the adsorbate structure is controlled by
interactions with the solvent rather than with the substrate.
Electrochemistry and bioelectrochemistry towards the single-molecule level: Theoretical notions and systems

Surface structures controlled at the nanometer and single-molecule levels, with functions crucially determined by interfacial electron transfer (ET) are broadly reported in recent years, with different kinds of electrochemically controlled nanoscale/single molecule systems. One is the broad class of metallic and semiconductor-based nanoparticles, nano-arrays, nanotubes, and nanopits. Others are based on self-assembled molecular monolayers. The latter extend to bioelectrochemical systems with redox metalloproteins and DNA-based molecules as targets. We overview here some recent achievements in areas of interfacial electrochemical ET systems, mapped to the nanoscale and single-molecule levels. Focus is on both experimental and theoretical studies in our group. Systems addressed are organized monolayers of redox active transition metal complexes, and metalloproteins and metalloenzymes on single-crystal Au(111)-electrode surfaces. These systems have been investigated by voltammetry, spectroscopy, microcantilever technology, and scanning probe microscopy. A class of Os-complexes has shown suitable as targets for electrochemical in situ scanning tunnelling microscopy (STM), with close to single-molecule scanning tunnelling spectroscopic (STS) features. Mapping of redox metalloproteins from the three major classes, i.e. blue copper proteins, heme proteins, and iron-sulfur proteins, at the monolayer and single-molecule levels have also been achieved. In situ STM and spectroscopy of redox molecules and biomolecules have been supported by new theoretical frames, which extend established theory of interfacial electrochemical ET. The electrochemical nanoscale and single-molecule systems discussed are compared with other recent nanoscale and single-molecule systems with conspicuous device-like properties, particularly unimolecular rectifiers and single-molecule transistors. Both of these show analogies to electrochemical in situ STM features of redox molecules and biomolecules.

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Albrecht, T. (Intern), Kuznetsov, A. (Ekstern), Grubb, M. (Intern), Hansen, A. (Ekstern), Wackerbarth, H. (Intern), Welinder, A. C. (Intern), Ulstrup, J. (Intern)
Pages: 3143-3159
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Main Research Area: Technical/natural sciences

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Issue number: 15
ISSN (Print): 0013-4686
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BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 4.74 SJR 1.357 SNIP 1.167
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.349 SNIP 1.344 CiteScore 4.86
Potential-induced structural transitions of DL-homocysteine monolayers on Au(111) electrode surfaces

Monolayers of homocysteine on Au(111)-surfaces have been investigated by voltammetry, in situ scanning tunnelling microscopy (STM) and subtractively normalised interfacial Fourier transform spectroscopy (SNIFTIRS). A pair of sharp voltammetric peaks build up in the potential range 0 to -0.1 V (vs. SCE) in phosphate buffer pH 7.7. The peak half-widths are about 25 mV at a scan rate of 10 mV s⁻¹. This is much smaller than for a one-electron Faradaic process (90.6 mV) under similar conditions. The coverage of homocysteine is 6.1 (+/- 0.2) x 10⁻¹⁰ Mol cm⁻², or 5.9 x 10⁻⁵ C cm⁻², from Au-S reductive desorption at -0.8 V (SCE) in 0.1 M NaOH, while the charge is only about 8 x 10⁻⁶ C cm⁻² (pH 7.7) for the 0 to -0.1 V peak. This suggests a capacitive origin. The peak potential and shape depend on pH. At pH 7.7 both cathodic and anodic peak currents reach a maximum, but drop at both higher and lower pH. The midpoint potential shows biphasic behaviour, decreasing linearly with increasing pH until pH 10.4 towards a constant value at higher pH. The cathodic and anodic peak charges decay at pH both higher and lower than 7.7. The homocysteine monolayer was investigated by in situ STM at different potentials at pH 7.7. The molecules pack into highly ordered domains around the
peak potential. High-resolution in situ STM reveals a (root 3 x 5) R30 degrees lattice with three homocysteine molecules in each unit cell. The adlayer changes into disordered structures on either side of the peak potential. This process is reversible. We propose that the voltammetric peaks are capacitive. The ordered domains are formed only around the potential of zero charge (pzc) and dissipate at potentials on either side of the peak, inducing mirror charge flow in the metallic electrode as the charged -COO- and -NH3+ groups approach the surface. No bands for carboxylate coordinated to the surface were observed in SNIFTIRS implying more subtle orientation changes of the charged groups on transcribing the voltammetric peak. This scenario is incorporated in a simple phenomenological model.

**General information**
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Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Demetriou, A. (Intern), Welinder, A. C. (Intern), Albrecht, T. (Intern), Nichols, R. (Ekstern), Ulstrup, J. (Intern)
Pages: 210-221
Publication date: 2005
Main Research Area: Technical/natural sciences

**Publication information**
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BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
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Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): SJR 0.635 SNIP 0.817 CiteScore 1.69
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.692 SNIP 0.897 CiteScore 1.73
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.663 SNIP 0.754 CiteScore 1.59
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.667 SNIP 0.732 CiteScore 1.75
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 0.856 SNIP 0.91 CiteScore 1.81
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 0.895 SNIP 0.892 CiteScore 1.89
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.968 SNIP 0.935
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 1.124 SNIP 0.942
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 1.191 SNIP 0.899
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 1.088 SNIP 0.861
Scopus rating (2006): SJR 1.087 SNIP 0.984
Web of Science (2006): Indexed yes
Self-Assembly of Biomolecules on Electrode Surfaces; Oligonucleotides, Amino Acids, and Proteins towards the Single-Molecule Level

Electrochemical and bioelectrochemical electron transfer towards the single-molecule level.

Electrochemistry and bioelectrochemistry towards the nanoscale and single-molecule levels: Theoretical notions and some systems.
Electron transfer and redox metalloenzyme catalysis at the single-molecule level

Voltammetry based on single-crystal, atomically-planar metal electrodes is novel in bioelectrochemistry. Together with in situ scanning tunneling microscopy (STM) directly in aqueous buffer, single-crystal voltammetry has disclosed new detail in molecular adsorption and interfacial electron transfer (ET). Image interpretation requires, however, theoretical support, as STM represents both electronic and topographic features. Molecules with accessible redox levels offer other insight into electron tunneling mechanisms, addressed in detail for ET metalloproteins. We present here in situ STM of the blue redox metalloenzyme copper nitrite reductase (Achromobacter xylosoxidans, AxCuNiR) on Au(111) electrode surfaces modified by a self-assembled cysteamine monolayer. AxCuNiR displays strong nitrite reduction waves in this environment. AxCuNiR/cysteamine/ Au(111) surfaces were imaged at KNO2 concentrations where most of the enzyme is in the enzyme-substrate bound state. Molecular resolution for both cysteamine/Au(111) and AxCuNiR/cysteamine/ Au(111) electrode surfaces was achieved. The enzyme coverage is about 1.5 x 10(-13) Mol cm(-2), which is low compared with an ideal close-packed monolayer. The adlayer behaves as an assembly of individual molecules, reflected in distributions of molecular appearance, although a number of molecules do show the triangular shape of the trimeric AxCuNiR structure. The apparent average molecular height is about 11 Angstrom. This suggests that details of electronic structures and larger assemblies are needed to disentangle enzyme mechanisms at the single-molecule level.
In situ STM imaging and direct electrochemistry of Pyrococcus furiosus ferredoxin assembled on thiolate-modified Au(111) surfaces

We have addressed here electron transfer (ET) of Pyrococcus furiosus ferredoxin (PfFd, 7.5 kDa) in both homogeneous solution using edge plane graphite (EPG) electrodes and in the adsorbed state by electrochemistry on surface-modified single-crystal Au(111) electrodes, as revealed by scanning tunneling microscopy under potential control (in situ STM). Direct ET between PfFd in phosphate buffer solution, pH 7.9, and EPG electrodes is observed in the presence of promoters. Neomycin gives rise to a pair of redox peaks with a formal potential of ca -430 mV (vs SCE), corresponding to [3Fe-4S](1+/0). The presence of an additional promoter, which can be propionic acid, alanine, or cysteine, induces a second pair of redox peaks at similar to -900 mV (vs SCE) arising from [3Fe-4S](0/1-). A robust neomycin-PfFd complex was detected by mass spectrometry. The results clearly favor an ET mechanism in which the promoting effect of small organic molecules is through formation of promoter-protein complexes. The interaction of PfFd with small organic molecules in homogeneous solution offers clues to confine the protein on the electrode surface modified by the same functional group monolayer and to address diffusionless direct electrochemistry, as well as surface microstructures of the protein monolayer. PfFd molecules were found to assemble on either mercaptopropionic acid (MPA) or cysteine-modified Au(111) surfaces in stable monolayers or submonolayers. Highly ordered (2\sqrt{3} \times 5)R30\textdegree cluster structures with six MPA molecules in each cluster were found by in situ STM. Individual PfFd molecules on the MPA layer are well resolved by in situ STM. Under Ar protection reversible cyclic voltammograms were obtained on PfFd-MPA/Au(111) and PfFd-cysteine/Au(111) electrodes with redox potentials of -220 and -201 mV (vs SCE), respectively, corresponding to the [Fe3S4](1+/0) couple. These values are shifted positively by 200 mV relative to homogeneous solution due to interactions between the promoting layers and the protein molecules. Possible mechanisms for such interactions and their ET patterns are discussed.

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Christensen, H. E. M. (Intern), Ooi, B. L. (Intern), Ulstrup, J. (Intern)
Pages: 10200-10207
Publication date: 2004
Main Research Area: Technical/natural sciences

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Interfacial electron transfer at the single molecule level.

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Publication date: 2004
Event: Paper presented at Imperial College, London, United Kingdom.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 178199
Publication: Research › Paper – Annual report year: 2004

Long-range order of organized oligonucleotide monolayers on Au(111) electrodes
Oligonucleotides modified by a hexamethylene linker group adsorb on gold electrodes via Au-S bond formation. We have obtained novel data for adsorption of thiol-modified (HS) single-strand HS-10A and double-stranded HS-10AT oligonucleotides and for analogous thiol-free 10A (A = adenine) and 10T (T = thymine) nonspecifically adsorbed as reference molecules. Mercaptohexanol has served as a second reference molecule. The data are based on cyclic and differential pulse voltammetry, interfacial capacitance data, and in situ scanning tunneling microscopy (STM) directly in an aqueous buffer solution, with electrochemical potential control of both the sample electrode and the tip. All the data are based on single-crystal, atomically planar Au(111)-electrode surfaces. The high sensitivity of such surfaces provides accurate HS-10A and HS-10AT electrode coverages on the basis of the reductive desorption of the Au-S bond. The coverage is high and in keeping with dense monolayers of adsorbed HS-10A and HS-10AT in an upright or tilted orientation, with the oligonucleotide backbone repelled from the strongly negatively charged electrode surface. Adsorbed thiol-free 10A only gives a Au(111)-reconstruction peak, while 10T shows a subtle pattern involving pronounced voltammetric adsorption peaks indicative of both nonspecific adsorption via single thymine units and potential-dependent structural reorganization in the surface layer. In situ STM supports these findings at the molecular level. In situ STM of HS-10A discloses large, highly ordered domains at strongly negative sample potentials. Reversible domain formation and disordering could, moreover, be controlled by an electrochemical potential variation in the negative and positive directions, respectively. 10A and 10T did not form ordered adsorbate domains, substantiating that domain formation rests on adsorption of thiol-modified oligonucleotide adsorption in an upright or tilted orientation. The comprehensive, high-resolution information reported may hold prospects for single-molecule electronic conduction and molecular-scale mapping of oligonucleotide hybridization.

General information
State: Published
Organisations: Department of Chemistry
Authors: Wackerbarth, H. (Intern), Grubb, M. (Intern), Zhang, J. (Intern), Hansen, A. G. (Intern), Ulstrup, J. (Intern)
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Publication date: 2004
Main Research Area: Technical/natural sciences

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BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
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Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.99 SJR 1.55 SNIP 1.188
Web of Science (2016): Indexed yes
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Scopus rating (2015): SJR 1.686 SNIP 1.308 CiteScore 4.33
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.816 SNIP 1.391 CiteScore 4.59
Monolayer electrochemistry of copper nitrite reductase on Au(111) electrodes.
Book of abstracts, p. O09 and invited talk (J. Zhang).

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Hansen, A. G. (Intern), Welinder, A. (Ekstern), Christensen, H. E. M. (Intern), Ulstrup, J. (Intern)
Publication date: 2004
Event: Abstract from Spring Meeting of the Int. Soc. Electrochemistry, Xiamen, China.
Main Research Area: Technical/natural sciences
Source: orbit
Thiol- and Disulfide-modified Oligonucleotide Monolayer Structures on Polycrystalline and Single-Crystal Au(111) Surfaces

General information
State: Published
Organisations: Department of Chemistry, Department of Micro- and Nanotechnology, Department of Physics
Pages: 474-481
Publication date: 2004
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Solid State Electrochemistry
Volume: 8
ISSN (Print): 1432-8488
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 2.26 SJR 0.662 SNIP 0.721
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.652 SNIP 0.679 CiteScore 2.18
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.834 SNIP 1.009 CiteScore 2.59
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.735 SNIP 0.926 CiteScore 2.25
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 0.88 SNIP 1.009 CiteScore 2.23
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 0.871 SNIP 1.002 CiteScore 2.28
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.9 SNIP 0.974
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.851 SNIP 0.908
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.754 SNIP 0.738
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 0.78 SNIP 0.776
Scopus rating (2006): SJR 0.773 SNIP 0.961
Adsorption and Interfacial Electron Transfer of Saccharomyces Cerevisiae: Yeast Cytochrome c Monolayers on Au(111) Electrodes

We have studied the adsorption and electron-transfer dynamics of Saccharomyces cerevisiae (yeast) iso-l-cytochrome c adsorbed on Au(III) electrodes in aqueous phosphate buffer media. This cytochrome possesses a thiol group dose to the protein surface (Cys102) suitable for linking the protein to gold without drastic protein unfolding. A comprehensive approach, based on linear sweep and differential pulse voltammetry, capacitance measurements, X-ray photoelectron spectroscopy (XPS), in situ scanning tunneling microscopy (STM), and microcantilever sensor (MCS) techniques has been used. The voltammetric data display a thiol reductive desorption signal corresponding to dase to monolayer coverage. Reductive desorption is also reflected in a capacitance peak. Voltammetric signals from the heme group in both native and partially denatured states could also be detected. XPS shows dear Au -S band formation, but this observation is not conclusive for aqueous buffer conditions, as the protein is extensively unfolded under ultrahigh vacuum conditions needed for XPS. In situ STM dosifies de ar sub-monolayer coverage to molecular resolution. Imaging is robust in a 0.2 V electrochemical potential range negative of the equilibrium potential of YCC, where the protein is electrochemically functional. The MCS data show tensile differential stress signals when YCC is adsorbed on a gold-coate d MCS, with distinguishable adsorption phases in the time range from <102 s to several thousand seconds. Comprehensive approaches to the mapping of adsorbed functional redox metalloproteins toward the single-molecule level, such as in the present study, will be important in the construction of nanoscale devices for multifarious biological and environmental screening.

General information
State: Published
Organisations: Department of Chemistry, Bioprobes, Department of Micro- and Nanotechnology, Department of Physics
Pages: 3419-3427
Publication date: 2003
Main Research Area: Technical/natural sciences

Publication information
Journal: Langmuir
Volume: 19
Issue number: 8
ISSN (Print): 0743-7463
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 3.99 SJR 1.55 SNIP 1.188
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 1.686 SNIP 1.308 CiteScore 4.33
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 1.816 SNIP 1.391 CiteScore 4.59
Catalytic monolayer voltammetry and in situ scanning tunneling microscopy of copper nitrite reductase on cysteamine-modified Au(111) electrodes

We have studied the adsorption and electrocatalysis of the redox metalloenzyme blue copper nitrite reductase from Achromobacter xylosoxidans (AxCuNiR) on single-crystal Au(111)-electrode surfaces modified by a self-assembled monolayer of cysteamine. A combination of cyclic voltammetry and in situ electrochemical scanning tunneling microscopy (in situ STM) directly in aqueous acetate buffer, pH 6.0 has been used. High-resolution in situ STM shows that cysteamine packs into ordered domains with strip features of a periodic distance of 11.7 +/- 0.3 Angstrom. No voltammetric signals of the nitrite substrate on this surface could be detected. A strong cathodic catalytic wave appears in the presence of nitrite. The catalytic current follows a Michaelis-Menten pattern with a Michaelis constant of K_m approximate to 44 muM, which is close to the value for AxCuNiR in homogeneous solution. The apparent catalytic rate constant based on a dense monolayer is k(cat) = 6-10 s(-1). This is significantly lower than two reported values of 185 s(-1) and 1400-1900 s(-1) for AxCuNiR in homogeneous solution. In situ STM of adsorbed AxCuNiR on the cysteamine-modified Au(111) surface suggests, however, that the coverage is low and the actual rate constant 120-220 s(-1) is much closer to the values in
homogeneous solution. The results show that AxCuNiR can be brought to immobilization in a functional state on suitably modified, well-defined, atomically planar Au(111)-electrode surfaces. This would be important for forthcoming biotechnology at the monolayer and toward the single-molecule level.
Electron transfer behaviour of biological macromolecules towards the single-molecule level

Redox metalloproteins immobilized on metallic surfaces in contact with aqueous biological media are important in many areas of pure and applied sciences. Redox metalloprotein films are currently being addressed by new approaches where biotechnology including modified and synthetic proteins is combined with state-of-the-art physical electrochemistry with emphasis on single-crystal, atomically planar electrode surfaces, in situ scanning tunnelling microscopy (STM) and other surface techniques. These approaches have brought bioelectrochemistry important steps forward towards the nanoscale and single-molecule levels. We discuss here these advances with reference to two specific redox metalloproteins, the blue single-copper protein Pseudomonas aeruginosa azurin and the single-haem protein Saccharomyces cerevisiae yeast cytochrome c, and a short oligonucleotide. Both proteins can be immobilized on Au(111) by chemisorption via exposed sulfur-containing residues. Voltammetric, interfacial capacitance, x-ray photoelectron spectroscopy and microcantilever sensor data, together with in situ STM with single-molecule resolution, all point to a coherent view of monolayer organization with protein electron transfer (ET) function retained. In situ STM can also address the microscopic mechanisms for electron tunnelling through the biomolecules and offers novel notions such as coherent multi-ET between the substrate and tip via the molecular redox levels. This differs in important respects from electrochemical ET at a single metal/electrolyte interface. Similar data for a short oligonucleotide immobilized on Au(111) show that oligonucleotides can be characterized with comparable detail, with novel perspectives for addressing DNA electronic conduction mechanisms and for biological screening towards the single-molecule level.

General information
State: Published
Organisations: Department of Chemistry, Department of Micro- and Nanotechnology
Authors: Zhang, J. (Intern), Grubb, M. (Intern), Hansen, A. G. (Intern), Kuznetsov, A. (Ekstern), Boisen, A. (Intern), Wackerbarth, H. (Intern), Ulstrup, J. (Intern)
Pages: S1873-S1890
Publication date: 2003
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of physics-condensed matter
Volume: 15
Issue number: 18
ISSN (Print): 0953-8984
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 1.89 SJR 0.881 SNIP 0.754
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.824 SNIP 0.754 CiteScore 1.65
In situ scanning tunnelling microscopy of redox molecules. Coherent electron transfer at large bias voltages

Theories of in situ scanning tunnelling microscopy (STM) of molecules with redox levels near the substrate and tip Fermi levels point to 'spectroscopic' current-overpotential features. Prominent features require a narrow 'probing tip', i.e. a small bias voltage, \( eV_{\text{bias}} \), compared with the molecular and solvent reorganisation Gibbs energy, \( E_r \). However, a large \( V_{\text{bias}} \) is frequently needed for stable imaging. This applies particularly to in situ STM of redox metalloproteins, emerging as a new approach to imaging of biological processes directly in aqueous medium. We provide first an extension of previous theoretical work on in situ STM of redox molecules, to large bias voltages, \( eV_{\text{bias}} \) \( > E_r \). Large bias voltages give tunnelling contrasts independent of the overpotential over a broad range, as both the oxidised and reduced redox levels are located within the 'energy tip' between the substrate and tip Fermi levels. STM here involves coherent two-step interfacial electron transfer between the redox level and the enclosing substrate and tip. We have also extended previous
experimental in situ STM studies of the blue copper protein Pseudomonas aeruginosa azurin, adsorbed on Au(111), to cover a broad tunnelling current-overpotential range at a constant (large) bias voltage of +0.2 V. The current is found to be constant over a 0.25 V overpotential range, which covers roughly the range where the oxidised and reduced redox levels are located within the energy tip. STM contrast and apparent adsorbate coverage decrease outside this range. This could reflect in part redox processes of azurin, but also tip-induced disassembly of the azurin monolayer.

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Kuznetsov, A. (Ekstern), Ulstrup, J. (Intern)
Pages: 133-146
Publication date: 2003
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Electroanalytical Chemistry
Volume: 541
ISSN (Print): 1572-6657
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): SJR 0.741 SNIP 0.844 CiteScore 2.97
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SNIP 0.88 SJR 0.723 CiteScore 2.73
BFI (2014): BFI-level 1
Scopus rating (2014): SNIP 0.954 SJR 0.835 CiteScore 2.81
BFI (2013): BFI-level 2
Scopus rating (2013): SNIP 1.099 SJR 0.912 CiteScore 2.92
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SNIP 1.023 SJR 1.081 CiteScore 2.72
ISI indexed (2012): ISI indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SNIP 1.125 SJR 1.066 CiteScore 2.89
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SNIP 1.108 SJR 1.157
BFI (2009): BFI-level 2
Scopus rating (2009): SNIP 1.12 SJR 1.012
BFI (2008): BFI-level 2
Scopus rating (2008): SNIP 1.135 SJR 1.26
Web of Science (2008): Indexed yes
Scopus rating (2007): SNIP 1.243 SJR 1.276
Web of Science (2007): Indexed yes
Scopus rating (2006): SNIP 1.293 SJR 1.366
Scopus rating (2005): SNIP 1.228 SJR 1.228
Scopus rating (2004): SNIP 1.471 SJR 1.316
Web of Science (2004): Indexed yes
Scopus rating (2003): SNIP 1.185 SJR 1.174
Web of Science (2003): Indexed yes
Scopus rating (2002): SNIP 1.278 SJR 1.3
Scopus rating (2001): SNIP 1.285 SJR 1.222
Monolayer Assemblies of a De Novo Designed 4-alpha-Helix Bundle Carboprotein and Its Sulfur Anchor Fragment on Au(111) Surfaces Addressed by Voltammetry and In Situ Scanning Tunneling Microscopy

Mapping and control of proteins and oligonucleotides on metallic and nonmetallic surfaces are important in many respects. Electrochemical techniques based on single-crystal electrodes and scanning probe microscopies directly in aqueous solution (in situ SPM) have recently opened perspectives for such mapping at a resolution that approaches the single-molecule level. De novo design of model proteins has evolved in parallel and holds promise for testing and controlling protein folding and for new tailored protein structural motifs. In this report we combine these two strategies. We present a scheme for the synthesis of a new 4-R-helix bundle carboprotein built on a galactopyranoside derivative with a thiol anchor aglycon suitable for surface immobilization on gold. The carboprotein with thiol anchor in monomeric and dimeric (disulfide) form, the thiol anchor alone, and a sulfur-free 4-R-helix bundle carboprotein without thiol anchor have been prepared and investigated for comparison. Cyclic and differential pulse voltammetry (DPV) of the proteins show desorption peaks around -750 mV (SCE), whereas the thiol anchor desorption peak is at -685 mV. The peaks are by far the highest for thiol monomeric 4-R-helix bundle carboprotein and the thiol anchor. This pattern is supported by capacitance data. The DPV and capacitance data for the thiolated 4-R-helix bundle carboproteins and the thiol anchor hold a strong Faradaic reductive desorption component as supported by X-ray photoelectron spectroscopy. The desorption peak of the sulfur-free 4-R-helix bundle carboprotein, however, also points to a capacitive component. In situ scanning tunneling microscopy (in situ STM) of the thiol anchor discloses an adlayer with small domains and single molecules ordered in pin-striped supramolecular structures. In situ STM of thiolated 4-R-helix bundle carboprotein monomer shows a dense monolayer in a broad potential range on the positive side of the desorption potential. The coverage decreases close to this potential and single-molecule structures become apparent. The in situ STM contrast is also strengthened, indicative of a new redox-based tunneling mechanism. The data overall suggest that single-molecule mapping of natural and synthetic proteins on well-characterized surfaces by electrochemistry and in situ STM is within reach.
Nanoscale and single-molecule interfacial electron transfer

Electrochemical science and technology in the 21st century have reached high levels of sophistication. A fundamental quantum mechanical theoretical frame for interfacial electrochemical electron transfer (ET) was introduced by Revaz Dogonadze. This frame has remained for four decades as a basis for comprehensive later theoretical work and data interpretation in many areas of chemistry, electrochemistry, and biology. We discuss here some new areas of theoretical electrochemical ET science, with focus on nanoscale electrochemical and bioelectrochemical sciences. Particular attention is given to in situ scanning tunneling microscopy (STM) and single-electron tunneling (SET, or Coulomb blockade) in electrochemical systems directly in aqueous electrolyte solution and at room temperature. We illustrate the new theoretical formalism and its perspectives by recent cases of electrochemical SET, negative differential resistance patterns, and by ET dynamics of organized assemblies of biological macromolecules, such as redox metalloproteins and oligonucleotides on single-crystal Au(III)-electrode surfaces.

General information

State: Published
Organisations: Department of Chemistry
Authors: Hansen, A. G. (Intern), Wackerbarth, H. (Intern), Nielsen, J. U. (Intern), Zhang, J. (Intern), Kuznetsov, A. (Ekstern), Ulstrup, J. (Intern)
Electronic Properties of Functional Biomolecules at Metal/Aqueous Solution Interfaces

Monolayers of molecules, which retain their function in the adsorbed state on solid surfaces, are important in materials science, analytical detection, and other technology approaching the nanoscale. Molecular monolayers, including layers of functional biological macromolecules, offer new insight in electronic properties and stochastic single-molecule features and can be probed by new methods which approach the single-molecule level. Olf of these is in situ scanning tunneling microscopy (STM) in which single-molecule electronic properties directly in aqueous solution are probed. In situ STM combined with physical electrochemistry, single-crystal electrodes, and spectroscopic methods is now a new dimension in interfacial bioelectrochemistry. We overview first same approaches to spectroscopic single-molecule imaging, including fluorescence spectroscopy, chemical reaction dynamics, atomic force microscopy, and electrochemical single-electron transfer. We then focus on in situ STM. In addition to high structural resolution, in situ STM offers a singlemolecule spectroscopic perspective. This emerges most clearly when adsorbate molecules contain accessible redox levels, and the tunneling current decomposes into successive single-molecule interfacial electron transfer (ET) steps. Theories of electrochemical ET and in situ STM of redox molecules as well as specific cases are addressed. Two-step in situ STM represents different molecular mechanisms and even new ET phenomena, related to coherent many-electron transfer. A number of systems are noted to accord with these views. The discussion is concluded by attention to Olle of the still very
few redox proteins addressed by in situ STM, the bine copper protein Pseudomonas aeruginosa azurin. Use of comprehensive electrochemical techniques has ascertained that well-defined protein monolayers in two opposite orientations can be formed and interfacial tunneling patterns disclosed. P. aeruginosa azurin emerges as by far the most convincing case where in situ STM of functional metalloproteins to single-molecule resolution has been achieved. This comprehensive approach holds promise for broader use of in situ STM as a single-molecule spectroscopy of metalloproteins and illuminates prerequisites and limitations of in situ STM of biological macromolecules.

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Kuznetsov, A. (Ekstern), Hansen, A. G. (Intern), Wackerbarth, H. (Intern), Christensen, H. E. M. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Pages: 1131-1152
Publication date: 2002
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Physical Chemistry Part B: Condensed Matter, Materials, Surfaces, Interfaces & Biophysical
Volume: 106
Issue number: 6
ISSN (Print): 1520-6106
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.367 SNIP 1.096 CiteScore 3.25
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.44 SNIP 1.14 CiteScore 3.28
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.494 SNIP 1.2 CiteScore 3.53
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.92 SNIP 1.251 CiteScore 3.66
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.78 SNIP 1.226 CiteScore 3.62
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.849 SNIP 1.214
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 2.232 SNIP 1.349
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 2.543 SNIP 1.381
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.346 SNIP 1.282
In situ Characterization of Monolayer of a de novo Designed 4-alpha-helix Bundle Carboprotein and Its Linker Group at The Single-Molecule Level.

**General information**
State: Published
Organisations: Department of Chemistry
Authors: Wackerbarth, H. (Intern), Brask, J. (Intern), Jensen, K. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Publication date: 2002
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 42905
Publication: Research › Poster – Annual report year: 2002

In situ STM and Nanoscale Electronic Function of Redox Metalloprotein Monolayers on Single-Crystal Au(111)-surfaces
Book of Abstract, 98.

**General information**
State: Published
Organisations: Department of Chemistry, Department of Micro- and Nanotechnology
Authors: Hansen, A. G. (Intern), Boisen, A. (Intern), Zhang, J. (Intern), Wackerbarth, H. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 2002
Event: Abstract from 21st European Congress on Surface Science and 7th International Conference on Nanometer-scale Science and Technology, Malmö, Sweden.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 39248
Publication: Research › Conference abstract for conference – Annual report year: 2002

Investigation of Redox Metalloproteins by Electrochemistry and Scanning Tunnelling Microscopy
Book of Abstract, p. 23.

**General information**
State: Published
Organisations: Department of Chemistry
Monolayers of a De Novo Designed 4-Alpha-Helix Bundle Carboprotein and Partial Structures on Au(111)-Surfaces

Mapping of structure and function of proteins adsorbed on solid surfaces is important in many contexts. Electrochemical techniques based on single-crystal metal surfaces and in situ scanning probe microscopies (SPM) have recently opened new perspectives for mapping at the single-molecule level. De novo design of model proteins has evolved in parallel and holds promise for test and control of protein folding and for new tailored protein structural motifs. These two strategies are combined in the present report. We present a synthetic scheme for a new 4alpha-helix bundle carboprotein built on a galactopyranoside derivative with a thiol anchor aglycon suitable for surface immobilization on gold. The galactopyranoside with thiol anchor and the thiol anchor alone were prepared for comparison. Voltammetry of the three molecules on Au(111) showed reductive desorption peaks caused by monolayer adsorption via thiolate-Au bonding. In situ STM of the thiol anchor disclosed an ordered adlayer with clear domains and molecular features. This holds promise, broadly for single-molecule voltammetry and the SPM and scanning tunnelling microscopy (STM) of natural and synthetic proteins.

General information
State: Published
Organisations: Department of Chemistry, NanoChemistry, Analytical Chemistry
Authors: Brask, J. (Intern), Wackerbarth, H. (Intern), Jensen, K. J. (Intern), Zhang, J. (Intern), Nielsen, J. U. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Pages: 27-32
Publication date: 2002
Main Research Area: Technical/natural sciences

Publication information
Journal: Bioelectrochemistry
Volume: 56
Issue number: 1-2
ISSN (Print): 1567-5394
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 3.45 SJR 0.751 SNIP 0.996
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.813 SNIP 1.383 CiteScore 3.76
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.115 SNIP 1.402 CiteScore 4.25
Organized monolayers of biological macromolecules on Au(111) surfaces

Single-crystal electrochemistry and scanning tunneling microscopy directly in aqueous electrolyte solution (in situ STM) are established in physical electrochemistry but new in studies of adsorption and interfacial electrochemistry of biological macromolecules. These high-resolution techniques have now been applied comprehensively to proteins and other biomolecules in recent studies, discussed in this report. Focus is on three systems. The first one is a pair of amino acids, cysteine and cystine. These are strongly adsorbed via thiolate and disulfide, respectively, with identical reductive desorption and in situ STM patterns. Long-range lateral order can be imaged to molecular resolution. The amino acids are also reference molecules for the blue single-copper protein Pseudomonas aeruginosa azurin. This protein assembles in two well-defined orientations. One applies on bare Au(111) to which the protein is linked via its surface disulfide group. This orients the copper center away from the electrode surface. The other mode is by hydrophobic interactions with variable-length alkanethiols self-assembled on Au(I 11). In this mode the copper center is directed towards the surface. Adsorption and long-range electron tunneling in both modes have been characterized in detail using different electrochemical and spectroscopic techniques, as well as STM. Other data show that penta-(A-T) oligonucleotide adsorbed via a covalently bound thiol linker also displays reductive desorption and in situ STM to molecular resolution. The three systems thus appear to open new perspectives for broader use of high-resolution electrochemical techniques in comprehensive investigations of large biological molecules.

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Nielsen, J. U. (Intern), Hansen, A. G. (Intern), Andersen, J. E. T. (Intern), Wackerbarth, H. (Intern), Ulstrup, J. (Intern)
Pages: 79-89
Deuterium isotope effect on the intramolecular electron transfer in Pseudomonas aeruginosa azurin

Intramolecular electron transfer in azurin in water and deuterium oxide has been studied over a broad temperature range. The kinetic deuterium isotope effect, k(H)/k(D), is smaller than unity (0.7 at 298 K), primarily caused by the different activation entropies in water (-56.5 J K\(^{-1}\) mol\(^{-1}\)) and in deuterium oxide (-35.7 J K\(^{-1}\) mol\(^{-1}\)). This difference suggests a role for distinct protein solvation in the two media, which is supported by the results of voltammetric measurements: the reduction potential (E\(^{0'}\)) of Cu2+/+ at 298 K is 10 mV more positive in D2O than in H2O. The temperature dependence of E\(^{0'}\) is also different, yielding entropy changes of -57 J K\(^{-1}\) mol\(^{-1}\) in water and -84 J K\(^{-1}\) mol\(^{-1}\) in deuterium oxide. The driving force difference of 10 mV is in keeping with the kinetic isotope effect, but the contribution to DeltaS^{double dagger} from the temperature dependence of E\(^{0'}\) is positive rather than negative. Isotope effects are, however, also inherent in the nuclear reorganization Gibbs free energy and in the tunneling factor for the electron transfer process. A slightly larger thermal protein expansion in H2O than in D2O (0.001 nm K\(^{-1}\)) is sufficient both to account for the activation entropy difference and to compensate for the different temperature dependencies of E\(^{0'}\). Thus, differences in driving force and thermal expansion appear as the most straightforward rationale for the observed isotope effect.

General information
State: Published
Organisations: Department of Chemistry
Authors: Farver, O. (Ekstern), Zhang, J. (Intern), Chi, Q. (Intern), Precht, I. (Ekstern), Ulstrup, J. (Intern)
Pages: 4426-4430
Publication date: 2001
Main Research Area: Technical/natural sciences

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Journal: PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES OF THE UNITED STATES OF AMERICA
Volume: 98
Issue number: 8
ISSN (Print): 0027-8424
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 8.56 SJR 6.321 SNIP 2.629
Web of Science (2016): Indexed yes
Electrochemistry of the blue copper protein Pseudomonas aeruginosa azurin

**General information**

State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Nielsen, J. U. (Intern), Hansen, A. G. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)

BFI (2015): BFI-level 2
Scopus rating (2015): SJR 6.767 SNIP 2.682 CiteScore 8.84
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 6.853 SNIP 2.725 CiteScore 8.86
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 6.989 SNIP 2.73 CiteScore 9.5
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 6.792 SNIP 2.682 CiteScore 9.49
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 6.771 SNIP 2.636 CiteScore 9.31
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SJR 6.769 SNIP 2.529
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 2
Scopus rating (2009): SJR 6.913 SNIP 2.544
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 2
Scopus rating (2008): SJR 6.899 SNIP 2.445
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 6.766 SNIP 2.441
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 6.734 SNIP 2.434
Web of Science (2006): Indexed yes
Scopus rating (2005): SJR 6.784 SNIP 2.551
Web of Science (2005): Indexed yes
Scopus rating (2004): SJR 7.026 SNIP 2.622
Web of Science (2004): Indexed yes
Scopus rating (2003): SJR 7.018 SNIP 2.501
Web of Science (2003): Indexed yes
Scopus rating (2002): SJR 7.183 SNIP 2.471
Web of Science (2002): Indexed yes
Scopus rating (2001): SJR 7.192 SNIP 2.463
Web of Science (2001): Indexed yes
Scopus rating (2000): SJR 7.731 SNIP 2.475
Web of Science (2000): Indexed yes
Scopus rating (1999): SJR 8.271 SNIP 2.446

Original language: English
Source: orbit
Source-ID: 46344
Publication: Research - peer-review › Journal article – Annual report year: 2001
Electrochemistry of the blue copper protein *Pseudomonas aeruginosa* azurin

**General information**

State: Published  
Organisations: Department of Chemistry  
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Nielsen, J. U. (Intern), Hansen, A. G. (Intern), Wackerbarth, H. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)  
Publication date: 2001  

Main Research Area: Technical/natural sciences  
Source: orbit  
Source-ID: 50551  
Publication: Research → Paper – Annual report year: 2001

Functional redox proteins on single-crystal gold electrodes: Some perspectives and puzzles.

**General information**

State: Published  
Organisations: Department of Chemistry  
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Nielsen, J. U. (Intern), Andersen, J. E. T. (Intern), Kuznetsov, A. M. (Ekstern), Ulstrup, J. (Intern)  
Publication date: 2001  

Main Research Area: Technical/natural sciences  
Source: orbit  
Source-ID: 50554  
Publication: Research → Paper – Annual report year: 2001

**Publication information**

Journal: ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY  
Volume: 222  
ISSN (Print): 0065-7727  
Ratings:  
Web of Science (2018): Indexed yes  
Web of Science (2017): Indexed Yes  
Scopus rating (2014): SJR 0.101 SNIP 0.013  
Web of Science (2014): Indexed yes  
Scopus rating (2013): SJR 0.101 SNIP 0.003  
Web of Science (2013): Indexed yes  
Scopus rating (2012): SJR 0.1 SNIP 0  
Scopus rating (2011): SJR 0.101 SNIP 0  
Web of Science (2011): Indexed yes  
Scopus rating (2010): SJR 0.101 SNIP 0  
Scopus rating (2009): SJR 0.101 SNIP 0  
BFI (2008): BFI-level 1  
Scopus rating (2008): SJR 0.101 SNIP 0  
Web of Science (2008): Indexed yes  
Scopus rating (2007): SJR 0.101 SNIP 0  
Scopus rating (2006): SJR 0.101  
Web of Science (2006): Indexed yes  
Scopus rating (2005): SJR 0.101  
Web of Science (2005): Indexed yes  
Scopus rating (2004): SJR 0.104 SNIP 0.028
Interfacial electron transfer and in situ scanning tunnelling microscopy of metalloprotein monolayers on single-crystal Au(111)

General information
State: Published
Organisations: Department of Chemistry
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 2001
Event: Abstract from Workshop on Nanoscale Biotechnology, Aalborg, Denmark.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 50542
Publication: Research - peer-review › Conference article – Annual report year: 2001

Monolayers of a de novo designed 4-alpha-helix bundlecarboprotein and partial structures on Au(111)-surfaces

General information
State: Published
Organisations: Department of Chemistry
Authors: Wackerbarth, H. (Intern), Brask, J. (Intern), Jensen, K. J. (Intern), Nielsen, J. U. (Intern), Zhang, J. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 2001
Event: Abstract from 10th International Conference on Bioinorganic Chemistry, Florence, Italy.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 43115
Publication: Research › Conference abstract for conference – Annual report year: 2001

Monolayers of a de novo designed 4-alpha-helix bundlecarboprotein and partial structures on Au(111)-surfaces

General information
State: Published
Organisations: Department of Chemistry
Authors: Wackerbarth, H. (Intern), Brask, J. (Intern), Jensen, K. J. (Intern), Nielsen, J. U. (Intern), Zhang, J. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 2001
Main Research Area: Technical/natural sciences
Journal: Journal of Inorganic Biochemistry
Volume: 86
Issue number: 1
ISSN (Print): 0162-0134
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
Ordered Assembly and Controlled Electron Transfer of the Blue Copper Protein Azurin at Gold (111) Single-Crystal Substrates

We have shown that Pseudomonas aeruginosa azurin can be immobilized on alkanethiol monolayers self-assembled on Au(111). Immobilization is achieved through hydrophobic interactions between the hydrophobic area around the copper atom in azurin and methyl heads of alkanethiol to form submonolayers or monolayers. In this orientation mode azurin molecules on Au(111) are oriented with the redox center (copper atom) facing the electrode surface. This is opposite to the orientation of azurin on bare gold which is via a surface disulfide group such as recently reported. Scanning tunneling microscopy (STM) with molecular resolution reveals that both well-ordered alkanethiol and protein adlayers are present. Adsorbed azurin molecules exhibit high stability and retain electron transfer (ET) function. Long-range interfacial ET between azurin and Au(111) across variable-length alkanethiol bridges was systematically investigated by different electrochemical techniques. Distance-dependent ET can be controlled by adjusting the length of the alkanethiol chain. The electrochemical ET rate constant is almost independent of the chain length up to ca. 9 methylene units but follows
exponential distance decay with a decay factor (beta) of 1.03 \pm 0.02 per CH2 unit at longer chain lengths. Overvoltage-dependent ET was also examined. The results provide a strategy to ordered molecular assemblies, and controlled orientation and ET of azurin at atomically planar metallic surfaces. This approach can in principle be extended to other redox metalloproteins.

**General information**

State: Published
Organisations: NanoChemistry, Department of Chemistry, Analytical Chemistry
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Pages: 4669-4679
Publication date: 2001
Main Research Area: Technical/natural sciences

**Publication information**
Journal: Journal of Physical Chemistry B
Volume: 105
Issue number: 20
ISSN (Print): 1520-6106
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 3.03 SJR 1.348 SNIP 1.02
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 1.367 SNIP 1.096 CiteScore 3.25
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 1.44 SNIP 1.14 CiteScore 3.28
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 1.494 SNIP 1.2 CiteScore 3.53
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.92 SNIP 1.251 CiteScore 3.66
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): SJR 1.78 SNIP 1.226 CiteScore 3.62
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 1.849 SNIP 1.214
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 2.232 SNIP 1.349
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 2.543 SNIP 1.381
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 2.346 SNIP 1.282
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 2.369 SNIP 1.415
Web of Science (2006): Indexed yes
We address the formation and characterisation of three different nanoscale systems on single-crystal Au(111) electrode surfaces in aqueous electrolyte solutions. The systems are investigated particularly by single-crystal electrochemistry and in situ scanning tunnelling microscopy (STM). The first system is the amino acid cystine in the adsorbed state. After dissociation of its disulfide bond cystine forms a highly ordered pattern controlled by adsorption via liberated sulfur atoms and intermolecular hydrogen bonding. Further organisation at three different levels by lateral interactions can be distinguished by the complementary use of single-crystal voltammetry and in situ STM. The second target molecule is the single-copper protein azurin which is shown to form monolayers which retain their long-range electron transfer function through the protein in the adsorbed state. The third system constitutes a new case for the use of in situ STM as a tool for manufacturing nanoscale pit structures on Au(111) surface at small bias voltage. Individually and in combination these data hold perspectives for preparation of atomically planar electrochemical surfaces with controlled functionalisation, orientation of functional biological macromolecules, nanoscale biological sensing, and controlled adsorption sites for enzymes and other reactive molecules.
Single-crystal electrochemistry and in situ scanning tunnelling microscopy of intermediate-size and large biomolecules

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Nielsen, J. U. (Intern), Wackerbarth, H. (Intern), Hansen, A. G. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 2001
Event: Abstract from XVI International Symposium on Bioelectrochemistry and Bioenergetics, Bratislava, Slovakia.
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 50540
Publication: Research › Conference abstract for conference – Annual report year: 2001

Voltammetry of native and recombinant Pseudomonas aeruginosa azurin on polycrystalline Au- and single-crystal Au(111)-surfaces modified by decanethiol monolayers

General information
State: Published
Organisations: Department of Chemistry
Authors: Fristrup, P. (Intern), Grubb, M. (Ekstern), Zhang, J. (Intern), Christensen, H. E. M. (Intern), Hansen, A. M. (Intern), Ulstrup, J. (Intern)
Pages: 128-133
Publication date: 2001
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of Electroanalytical Chemistry
Volume: 511
Issue number: 1-2
ISSN (Print): 1572-6657
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): SJR 0.741 SNIP 0.844 CiteScore 2.97
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SNIP 0.88 SJR 0.723 CiteScore 2.73
BFI (2014): BFI-level 1
Scopus rating (2014): SNIP 0.954 SJR 0.835 CiteScore 2.81
BFI (2013): BFI-level 2
Scopus rating (2013): SNIP 1.099 SJR 0.912 CiteScore 2.92
ISI indexed (2013): ISI indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SNIP 1.023 SJR 1.081 CiteScore 2.72
ISI indexed (2012): ISI indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SNIP 1.125 SJR 1.066 CiteScore 2.89
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Scopus rating (2010): SNIP 1.108 SJR 1.157
BFI (2009): BFI-level 2
Scopus rating (2009): SNIP 1.12 SJR 1.012
BFI (2008): BFI-level 2
Scopus rating (2008): SNIP 1.135 SJR 1.26
Creating Nanoscale Pits on Solid Surfaces in Aqueous Environment with Scanning Tunnelling Microscopy

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Department of Chemistry, Analytical Chemistry
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Friis, E. P. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Pages: L641-L648
Publication date: 2000
Main Research Area: Technical/natural sciences

Publication information
Journal: Surface Science
Volume: 463
ISSN (Print): 0039-6028
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 1.85 SJR 0.76 SNIP 0.859
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 1
Scopus rating (2015): SJR 0.764 SNIP 0.873 CiteScore 1.85
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 1
Scopus rating (2014): SJR 0.816 SNIP 0.888 CiteScore 1.81
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 1
Scopus rating (2013): SJR 0.824 SNIP 0.781 CiteScore 1.72
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): SJR 1.095 SNIP 0.888 CiteScore 1.91
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
METHOD FOR FABRICATING NANOSCALE PATTERNS ON A SURFACE

A novel method to fabricate nanoscale pits on Au(111) surfaces in contact with aqueous solution is claimed. The method uses in situ electrochemical scanning tunnelling microscopy with independent electrochemical substrate and tip potential control and very small bias voltages. This is significantly different from other documented methods, which mostly apply high and short voltage pulses. The most important advantages of the present method are that the high precision in aqueous environment so that nanopatterns of the pits can be designed, and that the operations are simple and require no instrumental accessories. Parameters, which control the pit formation and size, have been systematically characterized and show that the primary controlling parameter is the bias voltage. A mechanism based on local surface reconstruction induced by electronic contact between tip and substrate is in keeping with the overall patterns for pit formation. A range of potential applications is proposed.
Molecular monolayers and interfacial electron transfer of pseudomonas aeruginosa azurin on Au(111)

We provide a comprehensive approach to the formation and characterization of molecular monolayers of the blue copper protein Pseudomonas aeruginosa azurin on Au(111) in aqueous ammonium acetate solution. Main issues are adsorption patterns, reductive desorption, properties of the double layer, and long-range electrochemical electron transfer between the electrode and the copper center. Voltammetry, electrochemical impedance spectroscopy (EIS), in situ scanning tunneling microscopy (STM), and X-ray photoelectron spectroscopy (XPS) have been employed to disclose features of these issues. Zn-substituted azurin, cystine, and 1-butanol are investigated for comparison. Cyclic voltammetric and capacitance measurements show qualitatively that azurin is adsorbed at submicromolar concentrations over a broad potential range. The characteristics of reductive desorption suggest that azurin is adsorbed via its disulfide group to form a monolayer. The adsorption of this protein on Au(111) via a gold-sulfur binding mode is further supported by XPS measurements. In situ STM images with molecular resolution have been recorded and show a dense monolayer organization of adsorbed azurin molecules. Direct electron transfer (ET) between the copper atom of adsorbed azurin and the electrode has been revealed by differential pulse voltammetry. The rate constant is estimated from electrochemical impedance spectroscopy and shows that ET is compatible with a long-range ET mode such as that anticipated by theoretical frames. The results constitute the first case of an electrochemically functional redox protein monolayer at single-crystal metal electrodes.

General information
State: Published
Organisations: Department of Chemistry, Department of Chemistry, Department of Physics
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Nielsen, J. U. (Intern), Fris, E. P. (Intern), Chorkendorff, I. (Intern), Canters, G. W. (Ekstern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Pages: 4047-4055
Publication date: 2000
Main Research Area: Technical/natural sciences

Publication information
Journal: Journal of the American Chemical Society
Volume: 122
Issue number: 17
ISSN (Print): 0002-7863
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): CiteScore 13.18 SJR 7.368 SNIP 2.584
Web of Science (2016): Indexed yes
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 6.826 SNIP 2.632 CiteScore 12.81
Web of Science (2015): Indexed yes
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 6.273 SNIP 2.578 CiteScore 11.92
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 5.953 SNIP 2.455 CiteScore 11.38
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 6.141 SNIP 2.379 CiteScore 10.37
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 5.447 SNIP 2.336 CiteScore 9.94
Web of Science (2011): Indexed yes
BFI (2010): BFI-level 2
Nanoscale depression formation for substrate surface involves bringing immersed object proximal to surface of substrate by applying two sets of operating parameters

NOVELTY - An object, partially immersed into a liquid environment, is brought proximal to the surface of a substrate by applying two sets of operating parameters including a bias voltage, a tunnel current and a working potential. The bias voltage of one operating parameter is negative. USE - For substrate surface. ADVANTAGE - Controls pit size and pattern of nanoscale depression. DESCRIPTION OF DRAWING(S) - The figure shows the schematic drawing of a scanning tunneling microscope tip and a substrate during formation and imaging of nanopits.
An Approach to Long-Range Electron Transfer Mechanisms in Metalloproteins: In Situ Scanning Tunnelling Microscopy With Submolecular Resolution

General information
State: Published
Organisations: Department of Chemistry, Analytical Chemistry, Department of Chemistry, NanoChemistry, Russian Academy of Sciences
Authors: Friis, E. P. (Intern), Andersen, J. E. T. (Intern), Kharkasts, Y. (Ekstern), Kuznetsov, A. (Ekstern), Nichols, R. J. (Ekstern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Pages: 1379-1384
Publication date: 1999
Main Research Area: Technical/natural sciences

Publication information
Journal: Proceedings of the National Academy of Sciences USA
Volume: 96
Original language: English
Source-ID: 173826
Publication: Research - peer-review › Journal article – Annual report year: 1999

Electrochemistry of Self-Assembled Monolayers of the Blue Copper Protein Pseudomonas Aeruginosa Azurin on Au(111)

General information
State: Published
Organisations: NanoChemistry, Department of Chemistry, Department of Chemistry, Analytical Chemistry
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Friis, E. P. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Pages: 91-96
Publication date: 1999
Main Research Area: Technical/natural sciences

Publication information
Journal: Electrochemistry Communications
Volume: 1
ISSN (Print): 1388-2481
Ratings:
BFI (2018): BFI-level 1
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 1
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 1
Scopus rating (2016): CiteScore 4.53 SJR 1.618 SNIP 1.076
Fabrication of nanoscale patterns on solid surfaces in aqueous electrochemical environment by scanning tunnelling microscopy

General information
State: Published
Organisations: Department of Chemistry
Authors: Chi, Q. (Intern), Zhang, J. (Intern), Friis, E. P. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 1999

Host publication information
Title of host publication: Fabrication of nanoscale patterns on solid surfaces in aqueous electrochemical environment by scanning tunnelling microscopy
Place of publication: Changchun
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 174176
Images of analytical chemistry

General information
State: Published
Organisations: Department of Chemistry
Authors: Andersen, J. E. T. (Intern), Zhang, J. (Intern), Chi, Q. (Intern), Hansen, A. G. (Intern), Nielsen, J. U. (Intern), Ulstrup, J. (Intern), Boisen, A. (Intern), Jensenius, H. (Intern)
Pages: 22-25
Publication date: 1999
Main Research Area: Technical/natural sciences

Publication information
Journal: Chemistry in Denmark
Volume: 80
Original language: Danish
Source:orbit
Source-ID: 174177

In Situ Scanning Probe Microscopy and New Perspectives in Analytical Chemistry

General information
State: Published
Organisations: Department of Chemistry, Department of Chemistry, Department of Micro- and Nanotechnology
Authors: Andersen, J. E. T. (Intern), Zhang, J. (Intern), Chi, Q. (Intern), Hansen, A. G. (Intern), Nielsen, J. U. (Intern), Friis, E. P. (Intern), Ulstrup, J. (Intern), Boisen, A. (Intern), Jensenius, H. (Intern)
Pages: 665-674
Publication date: 1999
Main Research Area: Technical/natural sciences

Publication information
Journal: Trends in analytical chemistry
Volume: 18
Issue number: 11
ISSN (Print): 0165-9936
Ratings:
BFI (2018): BFI-level 2
Web of Science (2018): Indexed yes
BFI (2017): BFI-level 2
Web of Science (2017): Indexed Yes
BFI (2016): BFI-level 2
Scopus rating (2016): SJR 2.499 SNIP 2.402 CiteScore 8.09
BFI (2015): BFI-level 2
Scopus rating (2015): SJR 2.437 SNIP 2.322 CiteScore 7.24
BFI (2014): BFI-level 2
Scopus rating (2014): SJR 2.194 SNIP 2.253 CiteScore 6.54
Web of Science (2014): Indexed yes
BFI (2013): BFI-level 2
Scopus rating (2013): SJR 2.292 SNIP 2.204 CiteScore 6.47
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 2
Scopus rating (2012): SJR 2.346 SNIP 2.057 CiteScore 5.9
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 2
Scopus rating (2011): SJR 2.715 SNIP 2.084 CiteScore 6.52
Interfacial electron transfer in electrochemistry and in situ scanning tunnelling microscopy

General information
State: Published
Organisations: Department of Chemistry
Authors: Friis, E. P. (Intern), Thuesen, M. H. (Intern), Zhang, J. (Intern), Ulstrup, J. (Intern)
Pages: 115-129
Publication date: 1999

Host publication information
Title of host publication: Interfacial Electrochemistry. Theory, Experiment and Application, A. Wieczkowski
Place of publication: New York
Publisher: Marcel Dekker
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 173834
Publication: Education › Book chapter – Annual report year: 1999

Molecular nanometer scale assemblies controlled by in situ electrochemical scanning tunnelling microscopy

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Friis, E. P. (Intern), Nielsen, J. U. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 1999

Host publication information
Title of host publication: Molecular nanometer scale assemblies controlled by in situ electrochemical scanning tunnelling microscopy
Self-assembled monolayers of the blue copper protein Pseudomonas aeruginosa azurin on Au (111)

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Friis, E. P. (Intern), Hansen, A. G. (Intern), Nielsen, J. U. (Intern), Andersen, J. E. T. (Intern)
Publication date: 1999

Host publication information
Title of host publication: Self-assembled monolayers of the blue copper protein Pseudomonas aeruginosa azurin on Au (111)
Place of publication: Changchun
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 174179
Publication: Research › Article in proceedings – Annual report year: 1999

Self-assembled monolayers of the blue copper protein Pseudomonas aeruginosa azurin on Au(111) investigated by voltammetry and in situ scanning tunnelling microscopy

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Friis, E. P. (Intern), Hansen, A. G. (Intern), Nielsen, J. U. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 1999

Host publication information
Title of host publication: Keynote lecture
Place of publication: Pavia
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 174180
Publication: Research › Article in proceedings – Annual report year: 1999

Single-crystal electrochemistry and in situ scanning tunnelling microscopy of redox metalloproteins

General information
State: Published
Organisations: Department of Chemistry
Authors: Zhang, J. (Intern), Chi, Q. (Intern), Nielsen, J. U. (Intern), Andersen, J. E. T. (Intern), Ulstrup, J. (Intern)
Publication date: 1999

Host publication information
Title of host publication: Single-crystal electrochemistry and in situ scanning tunnelling microscopy of redox metalloproteins
Place of publication: Changchun
Main Research Area: Technical/natural sciences
Source: orbit
Source-ID: 174181
Publication: Research › Article in proceedings – Annual report year: 1999

Projects:
Novel Approaches to absolute structure

Department of Chemistry
Period: 15/05/2018 → 14/05/2021
Number of participants: 3
Phd Student:
Pedersen, Katja Desiree (Intern)
Supervisor:
Zhang, Jingdong (Intern)
Main Supervisor:
Gotfredsen, Charlotte Held (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU)
Project: PhD

Metal-organic frameworks derived non-noble metal catalysts for proton exchange membrane fuel cells

Department of Chemistry
Period: 01/09/2017 → 31/08/2020
Number of participants: 4
Phd Student:
Huang, Wei (Intern)
Supervisor:
Mølhave, Kristian (Intern)
Sun, Hongyu (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Stipendie fra udlandet
Project: PhD

Development of 3-demensional Graphene Biocatalysts for Enzymatic Biofuel Cells

Department of Chemistry
Period: 01/03/2017 → 29/02/2020
Number of participants: 3
Phd Student:
Tang, Jing (Intern)
Supervisor:
Engelbrekt, Christian (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Samfinansieret - Andet
Project: PhD

Development of NanoBiosensor for Detection of Food Contaminants

Department of Micro- and Nanotechnology
Period: 01/02/2017 → 31/01/2020
Number of participants: 5
Phd Student:
Feng, Xiaotong (Intern)
Supervisor:
Bang, Dang Duong (Intern)
Wolff, Anders (Intern)
Zhang, Jingdong (Intern)
Main Supervisor:
Sun, Yi (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Fonde
Project: PhD

Characterisation of Materials based on Graphene and Gold
Department of Chemistry
Period: 01/09/2016 → 31/08/2019
Number of participants: 3
Phd Student:
Nielsen, Frederick Stappen (Intern)
Supervisor:
Engelbrekt, Christian (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Samfinansierede - Virksomhed
Project: PhD

Long-range interfacial electron transfer between electrode and microorganisms
Department of Chemistry
Period: 15/08/2016 → 14/08/2019
Number of participants: 3
Phd Student:
Zheng, Zhiyong (Intern)
Supervisor:
Christensen, Hans Erik Mølager (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Stipendie fra udlandet
Project: PhD

In situ nanoscale investigation of microbial extracellular electron transfer
Department of Chemistry

NanoChemistry
Organic Chemistry
Period: 01/04/2016 → 31/03/2018
Number of participants: 2
Supervisor:
Erik Mølager Christensen , Hans (Ekstern)
Main Supervisor:
Zhang, Jingdong (Intern)

Porous Carbon Nanomaterials for Bioelectrochemistry
2-year postdoc project
Department of Chemistry
Nanoscale bioelectrochemistry for development of enzymatic fuel cells
Department of Chemistry
Period: 15/12/2015 → 14/12/2018
Number of participants: 3
Phd Student:
Shen, Fei (Intern)
Supervisor:
Ulstrup, Jens (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: Stipendie fra udlandet
Project: PhD

Development of quinones-enriched gold nanoparticles for energy storage and bioelectrochemistry
Department of Chemistry
NanoChemistry
Organic Chemistry
Period: 01/08/2015 → 31/07/2017
Number of participants: 4
Supervisor:
Ulstrup, Jens (Intern)
Tanner, David Ackland (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)
Project Coordinator:
Wagner, Michal (Intern)

Investigation of Bio-nano Materials Produced by Electrochemical Active Bacterial cells at Nanoscale
Department of Chemistry
NanoChemistry
Period: 15/07/2015 → 14/07/2016
Number of participants: 3
Supervisor:
Zhang, Jingdong (Intern)
Ulstrup, Jens (Intern)
Project Coordinator:
Wu, Ranran (Intern)
Three Dimensional Porous Nanoelectrodes for Efficient Energy Conversion
Department of Chemistry
NanoChemistry
Period: 01/01/2015 → 31/12/2015
Number of participants: 1
Project Coordinator:
Zhang, Jingdong (Intern)

Electronic properties and surface facet effects of noble metal and semiconductor nanocrystals as catalysts in pure and applied bioelectrochemistry
Department of Chemistry
NanoChemistry
Period: 01/01/2015 → 31/12/2016
Number of participants: 3
Supervisor:
Ulstrup, Jens (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)
Project Coordinator:
Zhang, Ling (Intern)

Chemical Production of 3D Graphene Biocatalysts for Enzymatic Biofuel Cells
Department of Chemistry
NanoChemistry
Period: 01/01/2015 → 31/12/2018
Number of participants: 3
Project participant:
Werchmeister, Rebecka Maria Larsen (Intern)
Shen, Fei (Intern)
Project Coordinator:
Zhang, Jingdong (Intern)

Chemical Production of Graphene Catalysts for Electrochemical Energy Conversion
Department of Chemistry
Period: 15/03/2014 → 13/11/2017
Number of participants: 6
Phd Student:
Seselj, Nedjeljko (Intern)
Supervisor:
Ulstrup, Jens (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)
Examiner:
Henriksen, Niels Engholm (Intern)
Nørgaard, Kasper (Ekstern)
Wollenberger, Ulla (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Samfinansieret - Andet

Relations
Publications:
Chemical Production of Graphene Catalysts for Electrochemical Energy Conversion

Project: PhD

Chemical Production of Graphene Catalysts for Electrochemical Energy Conversion

Department of Chemistry
NanoChemistry
Period: 01/01/2014 → 31/12/2016
Number of participants: 2
Project participant:
Seselj, Nedjeljko (Intern)
Project Coordinator:
Zhang, Jingdong (Intern)

Functional gold-based nanomaterials

Department of Chemistry
NanoChemistry
Period: 01/01/2014 → 31/12/2015
Number of participants: 1
Project Coordinator:
Zhang, Jingdong (Intern)

Investigation of Solid / Liquid Electrochemical Interfaces at Nanometer Scale

Department of Chemistry
NanoChemistry
Period: 01/01/2012 → 31/12/2014
Number of participants: 4
Project participant:
Engelbrekt, Christian (Intern)
Jensen, Palle Skovhus (Intern)
Dey, Ramendra Sundar (Intern)
Project Coordinator:
Zhang, Jingdong (Intern)

Green Synthesis, Characterization and Application of Metallic Nanostructures

Department of Chemistry
Period: 01/09/2011 → 26/11/2014
Number of participants: 6
Phd Student:
Engelbrekt, Christian (Intern)
Supervisor:
Ulstrup, Jens (Intern)
Main Supervisor:
Zhang, Jingdong (Intern)
Examiner:
Harris, Pernille (Intern)
Nielsen, Michael Brorson (Intern)
Ding, Yi (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: 1/3 FUU, 1/3 inst 1/3 Andet
Project: PhD
To explore large-scale and low-cost nano-processing technology and eventually to prepare a broad range of orderly nano-size functional structures

Department of Chemistry
NanoChemistry
Period: 01/02/2010 → 31/01/2011
Number of participants: 2
Project participant:
Hao, Xian (Intern)
Project Coordinator:
Zhang, Jingdong (Intern)
Project

Green Synthesis, Characterization and Application of Metallic Nanostructures

Department of Chemistry
NanoChemistry
Period: 01/01/2010 → 31/12/2012
Number of participants: 3
Project participant:
Engelbrekt, Christian (Intern)
Jensen, Palle Skovhus (Intern)
Project Coordinator:
Zhang, Jingdong (Intern)
Project

Biological Surfaces and Bacterial Biofilms Investigated by Atomic Force Microscopy

Department of Chemistry
Period: 01/03/2008 → 27/06/2012
Number of participants: 6
Phd Student:
Hu, Yifan (Intern)
Supervisor:
Zhang, Jingdong (Intern)
Main Supervisor:
Ulstrup, Jens (Intern)
Examiner:
Christensen, Hans Erik Mølager (Intern)
Arnebrant, Thomas (Ekstern)
Mortensen, John (Ekstern)

Financing sources
Source: Internal funding (public)
Name of research programme: Institut stipendie (DTU) Samf.
Project: PhD

Rationelt design af metalloproteiner af katalytisk relevans - syntese og karakterisering af molybdaenanalager af jern-svovl proteiner

Department of Chemistry
Period: 01/01/2007 → 01/09/2010
Number of participants: 8
Phd Student:
Kristensen, Jytte (Intern)
Supervisor:
Ooi, Bee Lean (Intern)
Ulstrup, Jens (Intern)
Insulins struktur og kemiske egenskaber i nanoskala og på det enkelte molekyldes niveau

Department of Chemistry
Period: 01/05/2005 → 17/06/2010
Number of participants: 7
Phd Student:
Welinder, Anna Christina (Intern)
Supervisor:
Steensgaard, Dorte B. (Ekstern)
Zhang, Jingdong (Intern)
Main Supervisor:
Ulstrup, Jens (Intern)
Examiner:
Molin, Søren (Intern)
Jensen, Knud Jørgen (Intern)
Nichols, Richard John (Intern)

Financing sources
Source: Internal funding (public)
Name of research programme: DTU-lønnet stipendie
Project: PhD

Electronic Processes in Nanoscale Systems
The aim of this new untraditional research is to disclose and map structure and electronic function of individual molecules and biological macromolecules at single-molecule level. The research rests on: Theory of Molecular Electron and proton Transport in Chemical and Biological Systems. State-of-the-art electrochemistry, and In Situ and Electrochemical Scanning Tunneling and Atomic Force Microscopy of Biological Macromolecules

Department of Chemistry
Period: 01/01/1994 → …
Number of participants: 12
Project participant:
Nielsen, Jens Ulrik (Intern)
Friis, Esben P. (Intern)
Iversen, Gitte (Intern)
Hansen, Allan Glargaard (Intern)
Jensen, Thomas Jon (Intern)
Andersen, Niels Højmark (Intern)
Zhang, Jingdong (Intern)
Chi, Qijin (Intern)
Jespersen, Lise-Lotte (Intern)
Andersen, Jens (Intern)
Christensen, Hans Erik Mølager (Intern)
Project Manager, organisational:
Ulstrup, Jens (Intern)
Bioinorganic Chemistry

Multifarious and sophisticated functions in the biological nature are associated with metal atoms. Striking examples are dioxygen transport and storage by hemoglobin and myoglobin, the biological nitrogen and sulphur cycles, biomineralization, or photosynthesis and respiration. The function of more than a third of all proteins is thus crucially determined by metals such as calcium, magnesium, iron, copper, zinc and molybdenum, but many other biological functions including all phases of DNA/RNA replication and transcription, macromolecular folding etc. are also associated with metals. The chemistry of metals in biological systems constitutes the new interdisciplinary science bioinorganic chemistry, which is rooted in inorganic chemistry but with broad interfaces to biochemistry, biophysics, and other sciences. Fundamental research is directed towards biological structure and function with technological and biotechnological perspectives for example in environmental science, metals in medicine, industrial catalysts, microbiological metal extraction, sensors, and molecular nanoscale science. Bioinorganic chemistry at Technical University of Denmark is centred at Department of Chemistry, with broad national and European networks. The research is supported by the Danish Technical Science Research Council, and by the European Union. Research organization, and recent results are detailed below.

Department of Chemistry
University of Copenhagen

A. N. Frumkin Institute of Electrochemistry

Period: 01/01/1993 → …
Number of participants: 14
Project participant:
Iversen, Gitte (Intern)
Jespersen, Lise-Lotte (Intern)
Andersen, Niels Højmark (Intern)
Jensen, Thomas Jon (Intern)
Friis, Esben P. (Intern)
Nielsen, Jens Ulrik (Intern)
Hansen, Allan Glargaard (Intern)
Zhang, Jingdong (Intern)
Chi, Qijin (Intern)
Christensen, Hans Erik Mølager (Intern)
Led, Dr. J.J. (Ekstern)
Kharkats, Prof. Yu.I. (Ekstern)
Kuznetsov, Prof. A.M. (Ekstern)
Project Manager, organisational:
Ulstrup, Jens (Intern)

Financing sources
Source: Udenfor rammen
Name of research programme: Ukendt
Amount: 250,000.00 Danish Kroner
Source: Udenfor rammen
Name of research programme: Ukendt
Amount: 50,000.00 Danish Kroner
Source: Udenfor rammen
Name of research programme: Ukendt
Amount: 50,000.00 Danish Kroner

Activities:

3D Graphene-Glucose Oxidase Bioanodes for Enzymatic Biofuel Cells
Period: 27 Nov 2017 → 28 Nov 2017
Jing Tang (Speaker)
Rebecka Maria Larsen Werchmeister (Other)
Jingdong Zhang (Other)
Department of Chemistry
Related event

**PhD Workshop on Bioanalysis**
27/11/2017 → 28/11/2017
Postdam, Germany
Activity: Talks and presentations › Conference presentations

"Application of Scanning Probe Microscopy in Bioelectrochemistry"
Period: 27 Nov 2017 → 28 Nov 2017
Jingdong Zhang (Guest lecturer)

Department of Chemistry
NanoChemistry
Organic Chemistry

**Description**
PhD Workshop on Bioanalysis, University of Potsdam, Germany

**Related external organisation**

**University of Potsdam**
Germany
Activity: Talks and presentations › Conference presentations

The Au-S bond in biomolecular adsorption and electrochemical electron transfer
M.J. Ford (Other)
N.S. Hush (Other)
S. Marcuccio (Other)
J.R. Reimers (Other)
Jens Ulstrup (Invited speaker)
Jingdong Zhang (Other)

Department of Chemistry
NanoChemistry
Organic Chemistry

**Description**
2nd Gerischer-Kolb Symposium, Modern Aspects of Bioelectrochemistry, International Bunsen Discussion Meeting, Schloss Reisensburg, Germany, October 11 - 13, 2017
Degree of recognition: International
Documents:
AbstractGerischer_KolbOct2017

**Related external organisation**

**University of Ulm**
Ulm, Germany
Activity: Talks and presentations › Conference presentations

**Forth EuCheMS Inorganic Chemistry Conference (EICC-4)**
Period: 2 Jul 2017 → 5 Jul 2017
Ranran Wu (Participant)
Electrochemical Catalysis of Inorganic Complex $K_4[Fe(CN)_6]$ by *Shewanella oneidensis* MR-1

The interaction between metal and bacteria is a universal and important biogeochemical process in environment. As a dissimilatory metal reduction bacteria, the electrochemical active bacteria *Shewanella oneidensis* MR-1 can transfer intracellular electrons to minerals. This ability is attributed to the redox proteins localized to the outer-membrane, for example, the MtiC, MtrB, MtrA and CymA. Here we investigate its electrochemical properties towards redox inorganic redox compounds. It shows strong electrocatalysis toward electrochemical oxidation of $K_4[Fe(CN)_6]$. As a redox molecule, $K_4[Fe(CN)_6]$ gives a pair of redox peaks on voltammetry on bare glassy carbon electrode (GCE), symmetric with ideal peak-peak separation of about 60 mV, indicating of a reversible one-electron transfer process (blue curve, Figure 1). Surprisingly, the presence of *Shewanella oneidensis* MR-1 on GCE results an asymmetric redox peak, with almost disappearance of the cathodic peak and strengthen of the anodic peak, which is a typical catalysis feature of electrochemical oxidation.

Further experiments show that *Shewanella oneidensis* MR-1 does not give such electrocatalysis to redox compounds such as Ru[(NH$_3$)$_6$]Cl$_3$ and Resorufin. Systematic study on the selectivity and electrocatalysis mechanisms of *Shewanella oneidensis* MR-1 are under investigation. The ability of *Shewanella oneidensis* MR-1 to catalyze redox action of inorganic metal complex compounds will provide an insight on metal cycles in nature.

Links:
http://www.eicc-4.dk/home.html

Related event
Forth EuCheMS Inorganic Chemistry Conference (EICC-4)
02/07/2017 → 05/07/2017
Copenhagen, Denmark
Activity: Attending an event › Participating in or organising a conference

Electrocatalysis of interfacial bioelectrochemical electron transfer processes at the single-molecule level
Period: 14 Sep 2011 → 17 Sep 2011
Jingdong Zhang (Keynote speaker)

Department of Chemistry
NanoChemistry

Description
The structure, two-dimensional surface organization, and electron transfer (ET) function of biological macromolecules and biomimetic molecules on solid surfaces can now be addressed at a degree of detail that reaches the level of the single molecule. ET metalloproteins such as blue copper, heme, and iron-sulfur proteins have thus become new target molecules for single-molecule electrochemical surface science. Redox molecules such as these are “smart” molecules in the sense that they can be brought to “do” something in their natural aqueous biological buffer environment. Scanning tunnelling and atomic force microscopy in aqueous biological media supported by theoretical frames are core approaches in these new areas. We overview here some new recent efforts in electrocatalysis of redox metalloenzymes and biomimetic metalloenzyme models also brought to the single-molecule level. Structures and enzyme mechanisms of these large and composite biomolecular entities give new challenges. We shall address: • Binding modes of molecular linkers on electrochemical Au(111)-electrode surfaces. • A biomimetic metalloenzyme unit – the [Mo3S4]3+/4+ cluster. • Interfacial bioelectrochemical catalysis by “normal” and “green” gold nanoparticles. • Single-molecule bioelectrocatalysis - multi-copper nitrite reductase and laccases.

Related event
alicante.pdf
Electronic single-molecule conductivity of redox proteins and metalloenzymes in biological media
Period: 22 Jun 2010 → 26 Jun 2010
Jingdong Zhang (Speaker)
Department of Chemistry
NanoChemistry

Description
Electronic single-molecule conductivity of redox proteins and metalloenzymes in biological media: Workshop on Transport Phenomena in Molecular Nanostructures. Book of abstracts
22/06/2010 → 26/06/2010
ETH Zürich CECAM (Centre Européen de Calcul Atomique et Moleculaire)

Related external organisation
ETH Zürich
Zürich, Switzerland
Activity: Talks and presentations › Conference presentations