Direct Oxidation of Ferredoxin at Modified Gold Electrodes

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Bioelectricity from a Photosynthetic Bacteria

- A nanoprobe is inserted into the chloroplast
- High energy electrons from photosynthesis are transferred to ferredoxin (Fd) and will be collected at the anode electrode in the chloroplast stroma.
- In the thylakoid space, electrons will recombine with oxygen and H+ to form water.

Question: What material should be used for the electrodes?

Choosing an Electrode

- Water formation has fast kinetics at a metal surface: Au and Pt are easy to use in fabrication of probes.
- Fd oxidation has slow kinetics at unmodified electrode surfaces, hence low charge transfer rates.
- Mediating the anode reaction or modifying the electrode surface can improve charge transfer rates.

- Carbon electrodes are not compatible with our current probe fabrication techniques.
- Probes will be used in vivo – addition of a mediator to cell chemistry is undesirable.
- Self-assembled monolayers on gold are compatible with our fabrication process and do not require alteration of cellular solution chemistry.

Functionalizing Gold to Oxidize Ferredoxin

- Oxidation occurs at N atoms (*) at isoalloxazine end of FAD.

Oxidizing Ferredoxin

- C. reinhardtii and spinach Fd proteins both have 2Fe-2S clusters.
- FNR accepts the e- from two Fd before and donates to NADP+.
- FAD is the reaction site in FNR.

Emulation of FAD Active Region

- Pyridine approximates active region in FAD.
- Gold-sulfur has a strong covalent bond.
- Quantum chemical simulations indicate that oxidation of Fd by 4-PyS is possible. (See Steve Walsh’s poster, “Making Studies of Electron Transfer Processes in Photosynthesis”)

Electrode Preparation

1. 100nm Au evaporated on V1 mica with 5nm Ti adhesion layer. 2. Gold electrode annealed in H\textsubscript{2}/O\textsubscript{2} flame. 3. PyS monolayer self-assembled [Procedure previously described by Sawaguchi et al., Electrochimica Acta 45 (2000)]. 4. Electrode rinsed in ultrapure water and dried in air.

Electrode Surface Analysis

- Contact angle with water
- Decrease in contact angle is due to a decrease in hydrophobicity

X-ray Photoemission Spectroscopy (XPS)

- Emitted electrons give elemental composition.
- Angle-resolved measurements give relative coverage of layers.

Conclusion

- PyS self-assembled at pH ~1 appears to improve reduction and oxidation, but both peaks are overshadowed by other reactions (such as oxidation of dithionite and reduction of O\textsubscript{2}).
- pH 5 self-assembly solution does not reliably improve Fd oxidation rate at Au.
- Other surface modifiers may further improve kinetics: FAD can be attached to gold via PQQ and cysteamine thiol. Previously used to study glucose oxidase.