Artificial Photosynthesis: Mimicking Nature's Electronics for CO_2 fixation.

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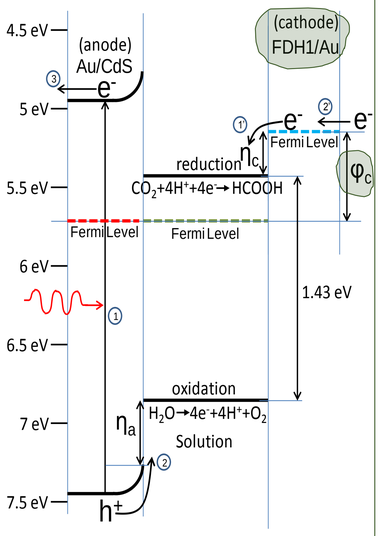
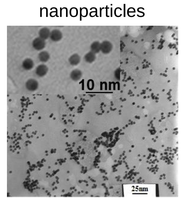
Device principle

1) Light exposure of the Cadmium sulfate (CdS) nanoparticles will excite electrons from the valence band to the conduction band. The "holes" (h^+) created will hydrolyze the water. The obtained high energy electrons and the hydrogen ions (H^+) will then participate in the reduction of CO_2 at the cathode
2) To avoid energy losses the electron transport will be regulated by networked nanoparticle arrays with a tunable band gap. Current flows between the electrodes once the potential difference between the electrodes crosses a threshold voltage.
3) At the cathode, formate dehydrogenase (FDH) will be the catalyst for the reduction of CO_2 to formate.

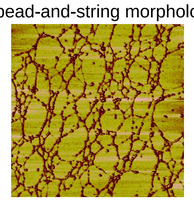


1) Photoactive CdS nanoparticles (Anode)

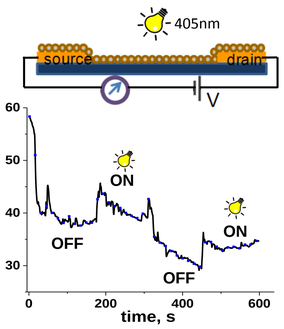
TEM image of highly monodisperse CdS nanoparticles



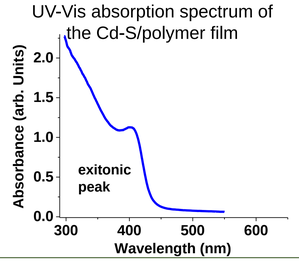
AFM image (2x2 µm) of nanoparticle precipitation in polyelectrolyte forming a bead-and-string morphology



The CdS/polymer conductive film is tested for photo-activity by recording the current increment once the film is exposed to light

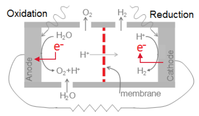


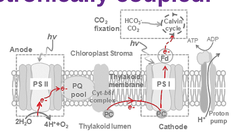
UV-Vis absorption spectrum of the Cd-S/polymer film



Motivation

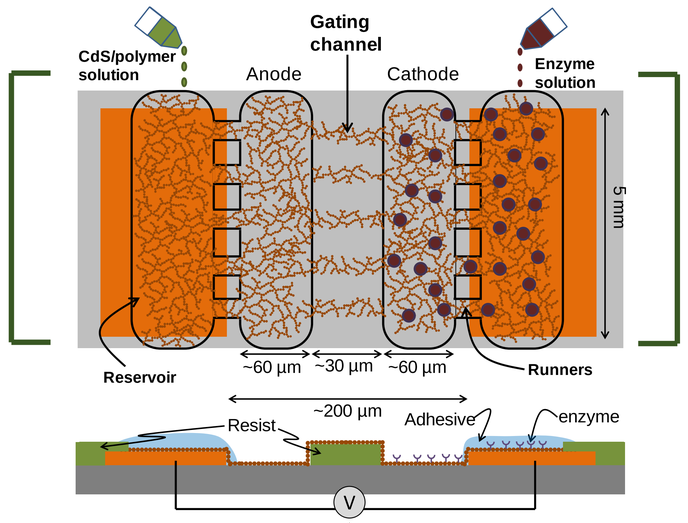
In conventional artificial photosynthesis cells, the electron transport is regulated by a permeable membrane that controls the diffusion of hydrogen. In this case the circuit is **ionically coupled.** However, in nature the electron transport during the photosynthesis is regulated by a series of enzymes in the thylakoid membrane, making the process **electronically coupled.**





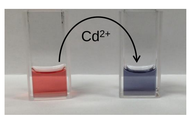
Goal: Design, study, and develop a device where the **coupling** between cathode and anode **is electronic**, such that, water is oxidized at the anode to drive CO_2 fixation at the cathode to form formate.

Proposed device

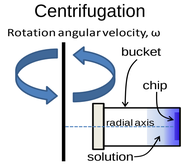


2) Gold Nanoparticle Necklaces (Gating channel)

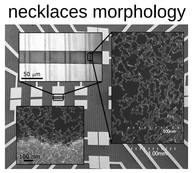
Gold nanoparticle necklace formation: Directed Self-Assembly

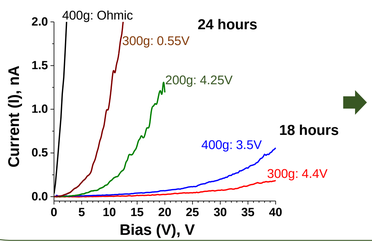


Necklace Deposition: Centrifugation



SEM image of Au nanoparticle necklaces morphology





Electrical properties of the gating channel for different conditions of formation.

The band-gap of the gating channel can be controlled by regulating direct assembly time and centrifugation speed for fixed deposition time of 5 min

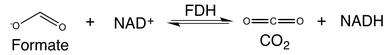
Conclusions

- A photosensitive electrode using a coating of polymer embedded with monodispersed CdS nanoparticle is an appropriate material to initiate the redox reaction stimulated by light.
- Nanoparticle necklace network will provide gated coupling between the cathode and anode.
- It is possible to fabricate a catalytic enzyme electrode by immobilizing FDH on nanoparticle necklace array.

3) Enzyme for CO_2 fixation (Cathode)

- FDH enzymes are expressed in two classes: (1) metal-free enzymes that strongly favor formate oxidation to CO_2 (endogenously expressed in *Candida boidinii*), and (2) W- or Mo-containing enzymes with activity in both formate oxidation and CO_2 reduction (endogenously expressed in *Clostridium carboxidivorans* and *Rhodobacter capsulatus*).

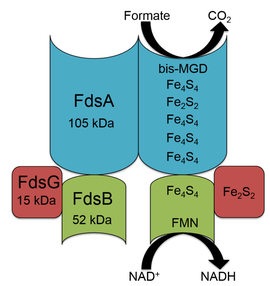
FDH catalysis (forward reaction: formate oxidation, reverse reaction: CO_2 reduction)



In vitro specific activity of FDH enzymes in formate oxidation and CO_2 reduction

Native FDH Organism	Formate Oxidation Specific Activity (U/mg)	CO_2 Reduction Specific Activity (U/mg)
Candida boidinii	2.08	N/A
Clostridium carboxidivorans	0.00206	0.00241
Rhodobacter capsulatus	0.104	**0.00682**

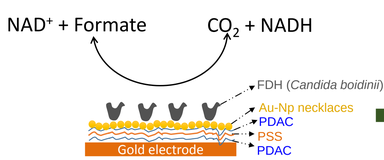
R. capsulatus FDH catalysis schematic



Target enzyme for future work

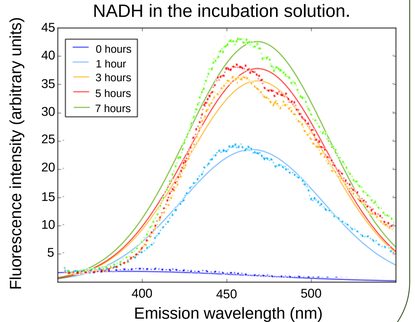
- FDH form *Candida boidinii* was used for immobilization trials as it is the most stable among the proposed enzymes even though its CO_2 reduction activity is not favorable.

Enzyme immobilization on polyelectrolytes/ Au nanoparticle necklaces film



Enzyme activity assay after immobilization: the electrode with immobilized enzyme was immersed in incubation solution containing NAD+ and formate.

Enzyme activity was confirmed by measuring the emission spectra at 340 nm excitation of NADH in the incubation solution.



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