



Electrocatalytic H₂ Production by Cobaloximes

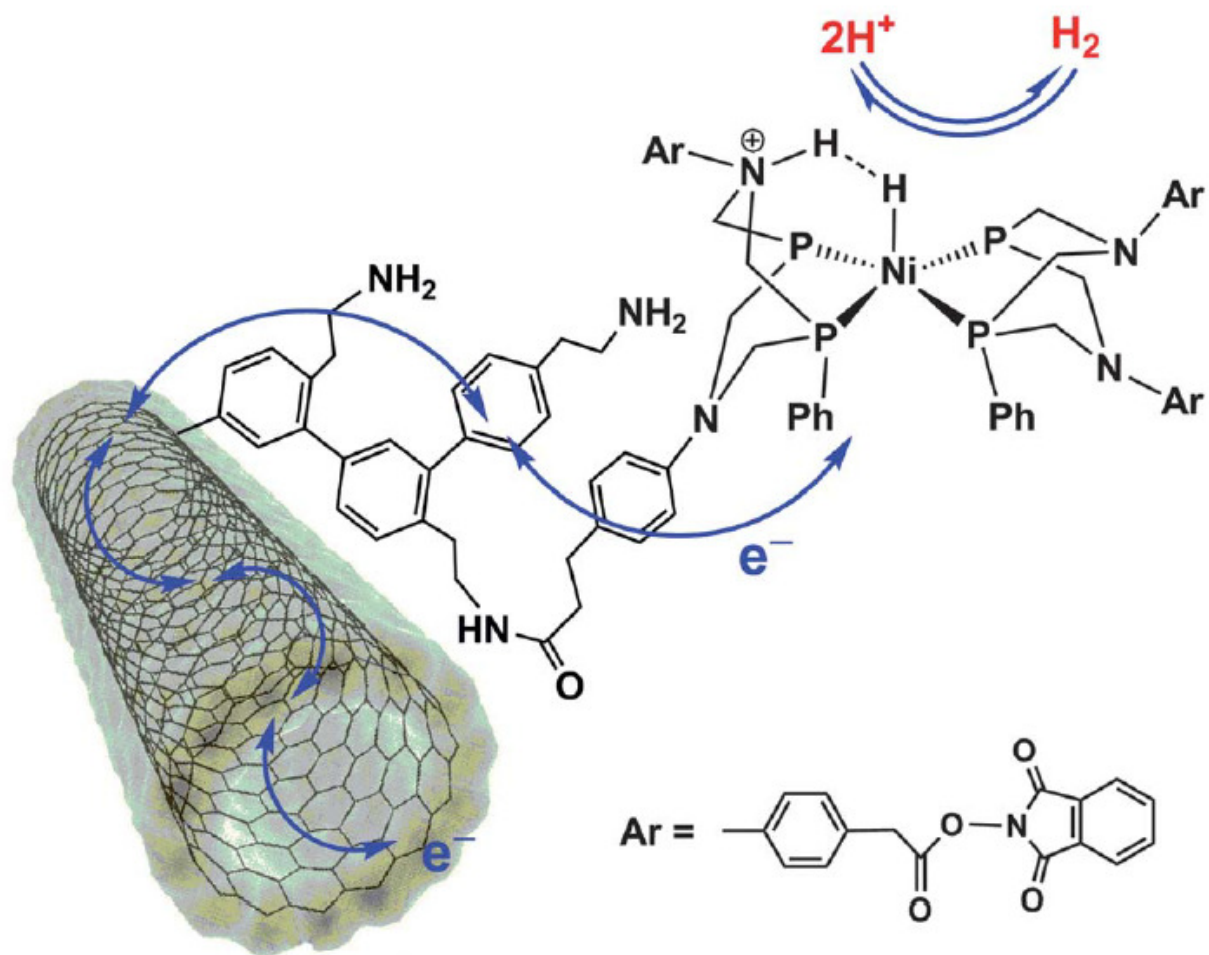
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Catalysis Basics

- The cobaloxime catalyst we will study is termed a ***homogeneous catalyst*** as it is dissolved in the same solvent as the substrate (H^+).
- In contrast, ***heterogeneous catalysts***, such as *palladium on carbon*, are insoluble and must adsorb the substrate from solution at its surface.

Catalytic mechanisms are considerably easier to study in homogeneous systems, where such powerful methods as NMR can be used to both assign structures and follow reaction kinetics.

- Homogeneous catalysts have the disadvantage that they can be difficult to separate from the product.
- Homogeneous catalysts can also be chemically grafted on to solid supports for greater ease of separation of the catalyst from the reaction products.
- Although the catalyst is now technically heterogeneous, it often retains the characteristic reactivity pattern that it showed as a homogeneous catalyst, and its properties are usually distinct from those of any of the classical heterogeneous catalysts—these are sometimes called ***“heterogenized” homogeneous catalysts***.



Example of a heterogenized Ni phosphine H^+ reduction catalyst

- The mechanistic ideas developed in **homogeneous catalysis are also becoming more influential** in the field of classical heterogeneous catalysis by suggesting structures for intermediates and mechanisms for reaction steps.
- By bringing about a reaction at **lower temperature**, a catalyst can **save energy** in commercial applications. It often gives **higher selectivity** for the desired product, minimizing product separation problems and **avoiding the need to discard the undesired product as waste**.
- Environmental concerns have promoted the idea of **atom economy**, which values a process most highly when all the atoms in the reagents are used to form the product, minimizing waste.
- The selectivity can be controlled by altering the ligands, allowing synthesis of products not formed in the un-catalyzed process.
- With growing regulatory pressure to synthesize drugs in enantiopure form, asymmetric catalysis has come to the fore, along with enzyme catalysis, as the only practical way to make such products on a large scale.

CATALYSIS IS GREEN CHEMISTRY !!!



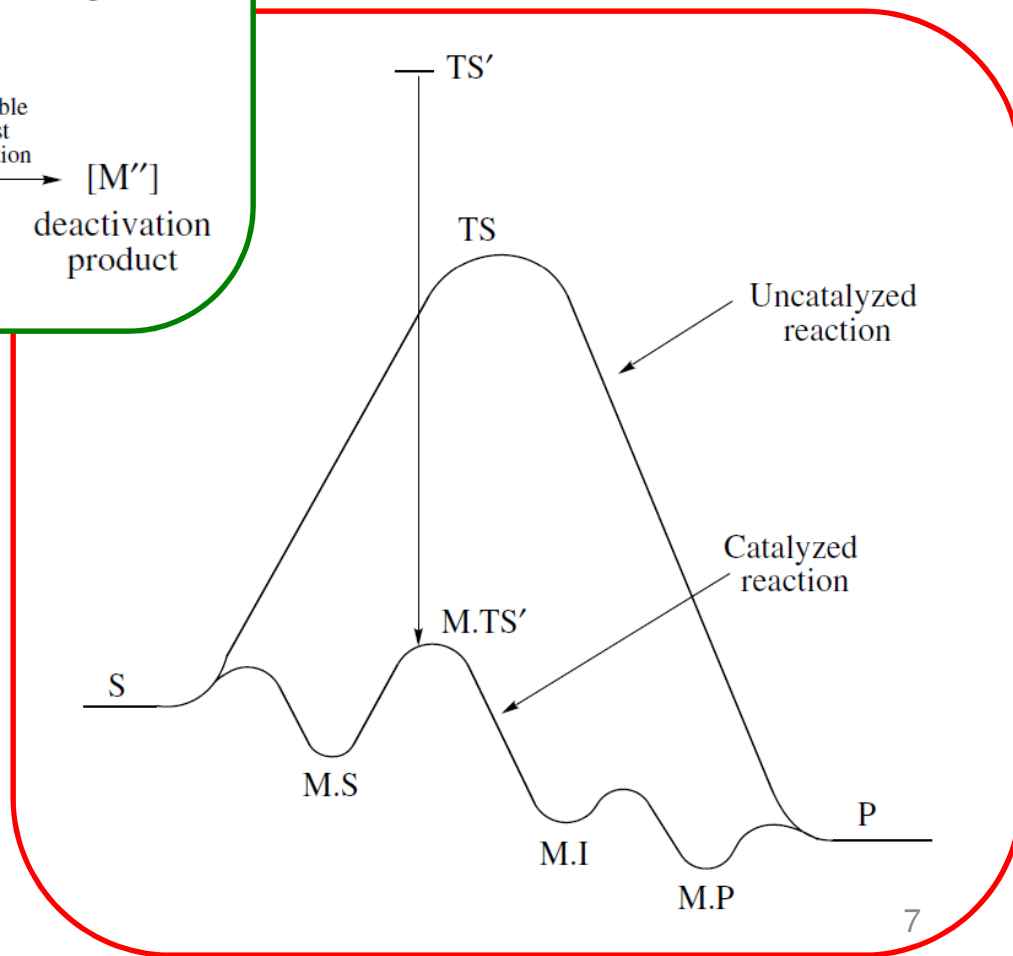
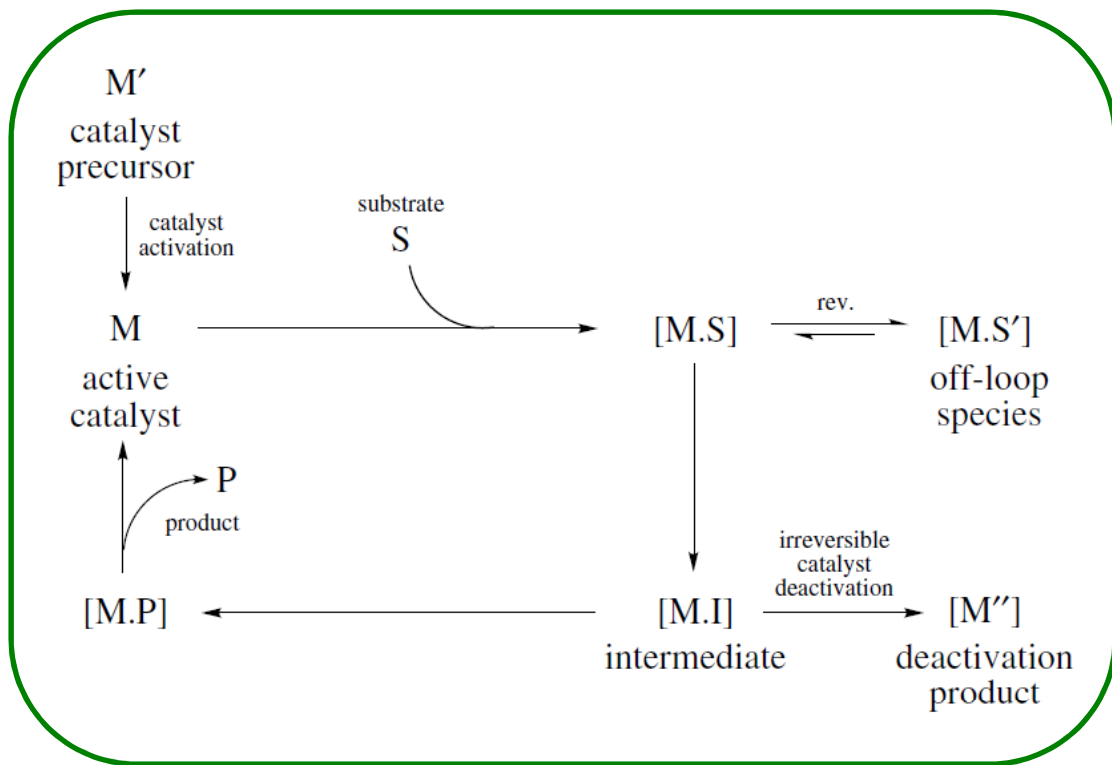
- A catalyst may be defined by its **Turnover Number (TN)**. Each time the complete catalyst cycle occurs, we consider one catalytic turnover to have been completed.

$$\text{Turnover Number (TN)} = \frac{\text{moles of product formed}}{\text{moles of catalyst}}$$

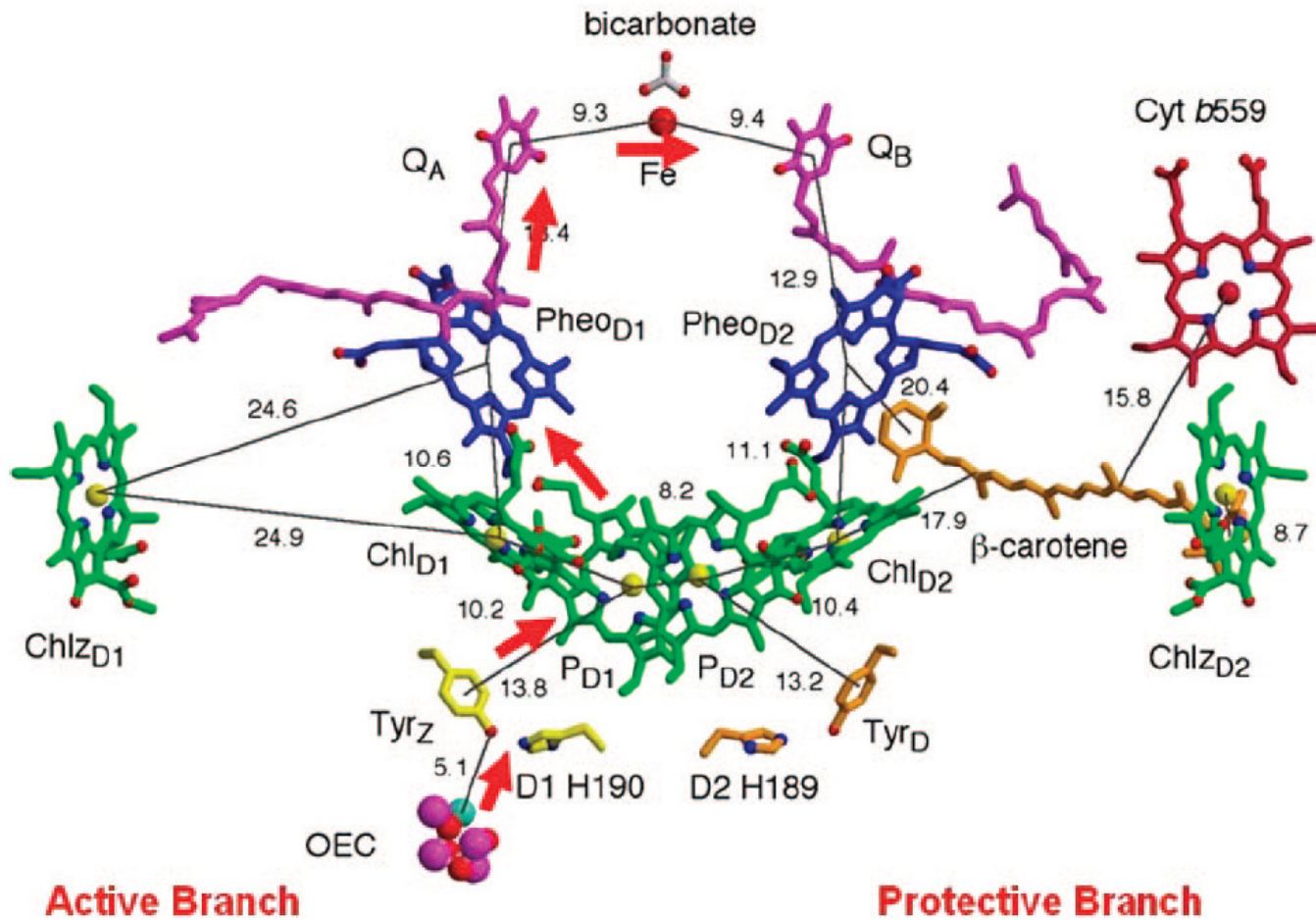
- The **lifetime of the catalyst** before deactivation or decomposition is quantified using TN.
- The catalytic rate can be conveniently given in terms of the **Turnover Frequency (TOF)** measured in turnovers per unit time (often per hour).

$$\text{Turnover Frequency (TOF)} = \frac{\text{moles of product formed}}{\text{hour}}$$

- For most transition metal catalysts, the catalyzed **pathway is completely changed** from the pathway of the uncatalyzed reaction. Instead of passing by way of the high-energy uncatalyzed transition state TS, the catalyzed reaction normally goes by a multistep mechanism in which the metal stabilizes intermediates that are stable only when bound to the metal.
- Normally, the catalyst only increases the rate of a process but **does not alter its position of equilibrium**, which is decided by the relative thermodynamic stabilities of substrate and products.
- For example, if the substrate S is slightly less stable than the product P, so the reaction will eventually reach an equilibrium favoring P.



Electron Transfer - PSII reaction center



- Electronic excitation of the dimer leads to a primary charge separation within a very short time.

Solar Driven Water Splitting

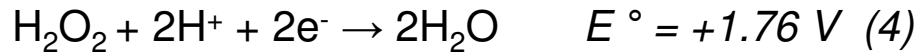
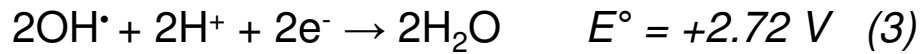
proton
reduction

+

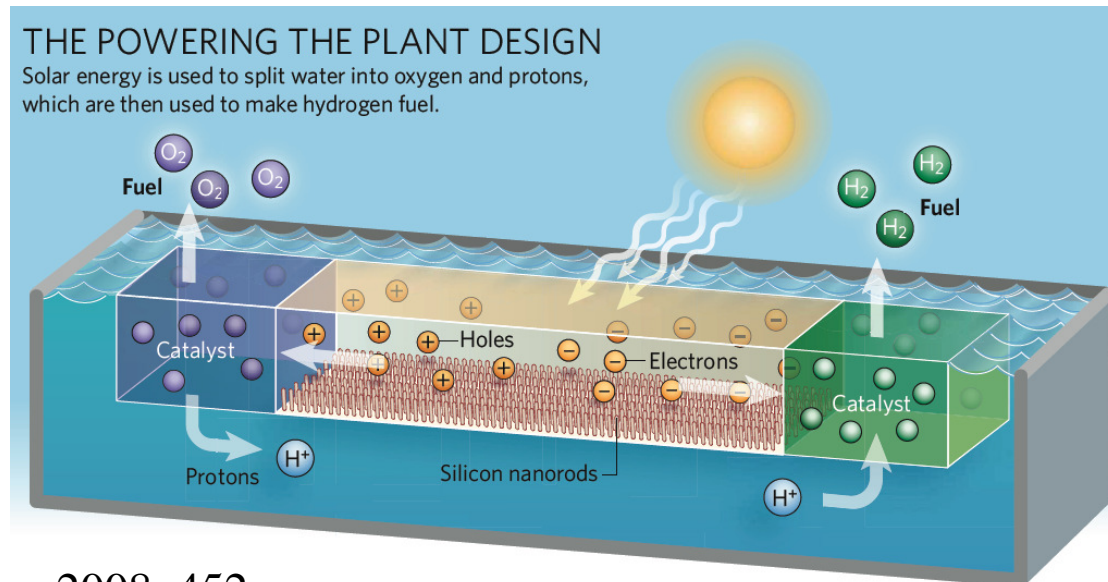
water
oxidation



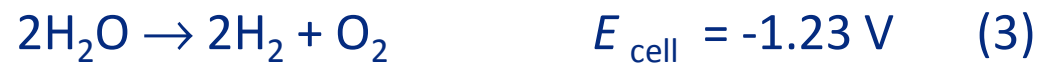
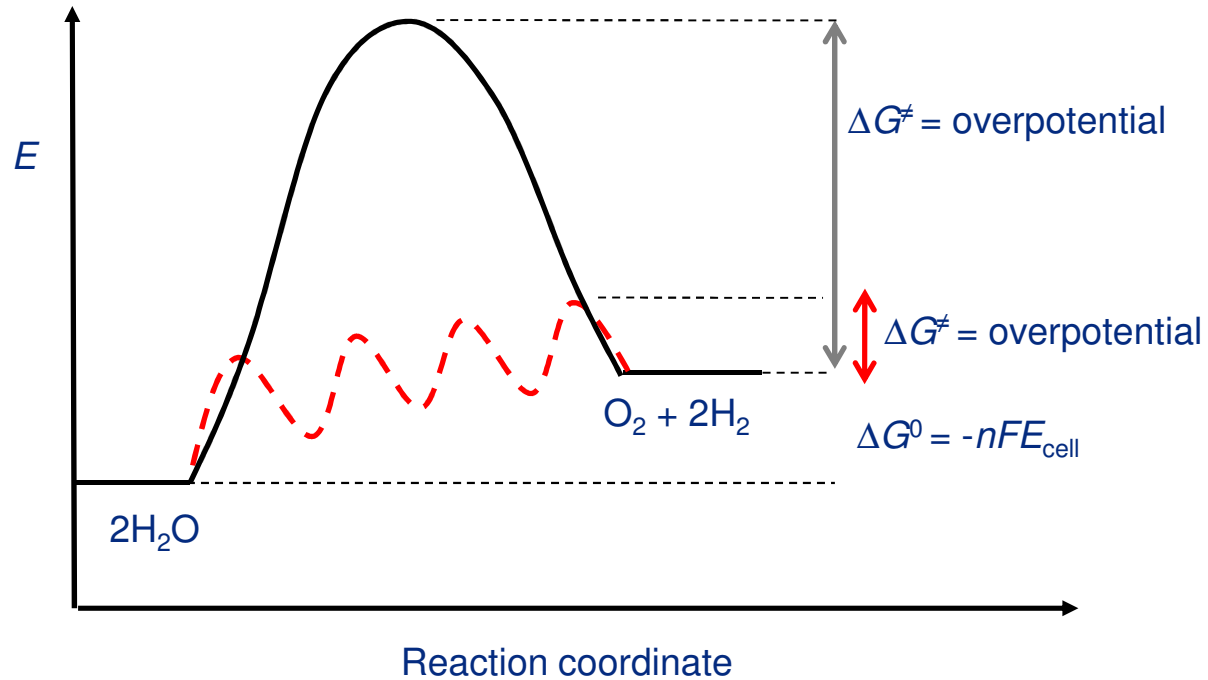
overall
water
splitting



(E° @ pH 0 vs. NHE)



Water Oxidation = Fuel Cell



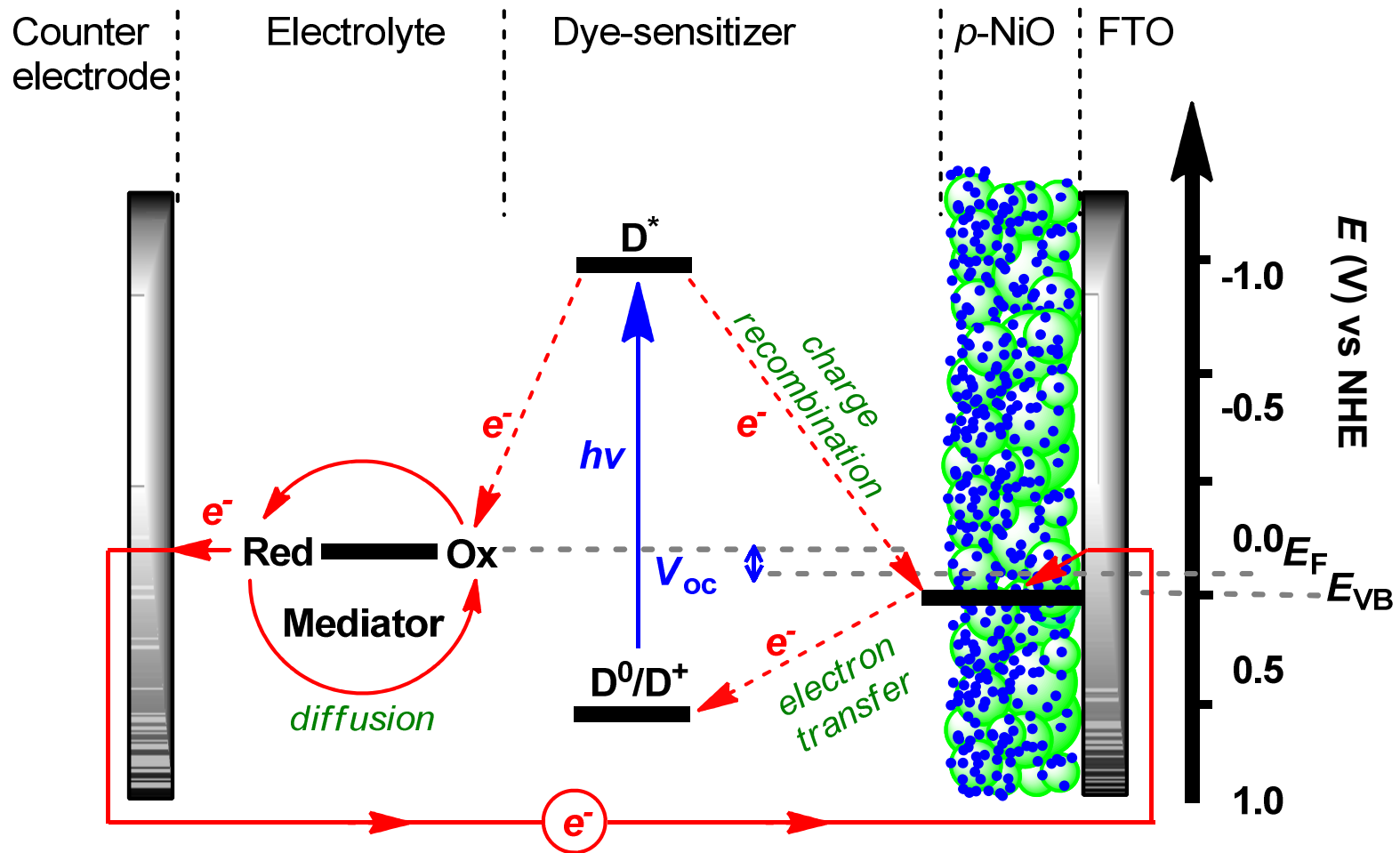
$$\Delta G^0 = +237 \text{ kJ mol}^{-1}$$

Catalyst Criteria & Overpotential

- Any promising H₂-evolving electrocatalysts should have the following properties:
 - a high catalytic activity
 - low overpotential
 - highly robust or regenerative
 - cheap to produce
- The catalytic activity and the overpotential are two inseparable criteria for evaluating catalyst systems used for electrochemical H₂ production.
- Earth-abundant (first row transition) metal molecular catalysts are only highly active at large overpotentials.
- Catalysts working at low overpotentials typically display poor efficiencies.

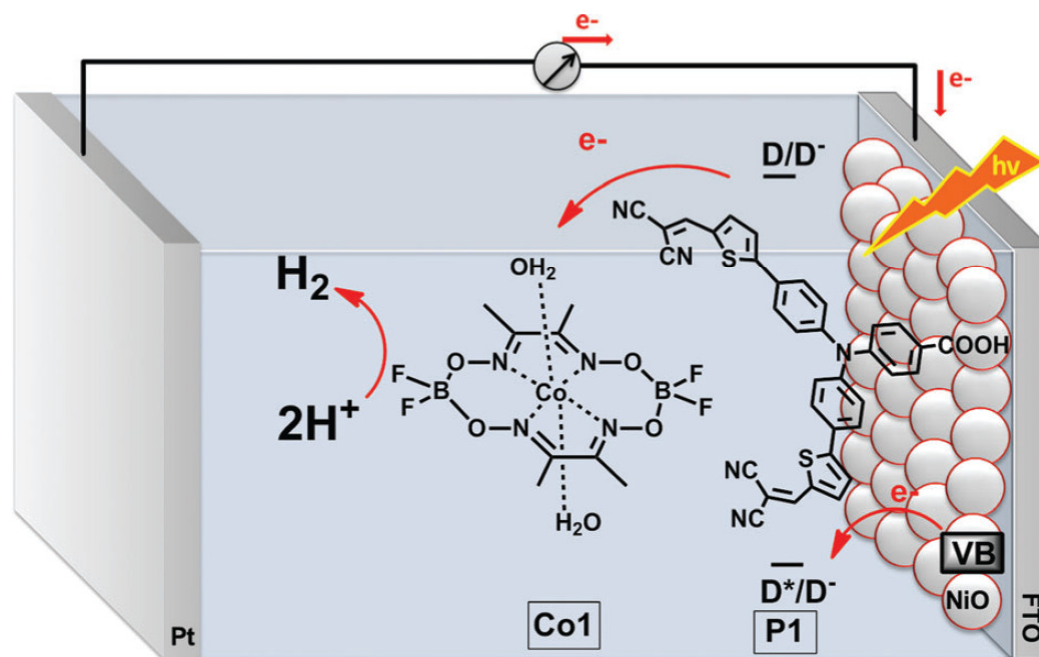
p-Type DSSCs (reverse Gratzel cell)

- Can we take a similar approach to *p*-type DSSCs ?



Visible light driven hydrogen production from a photo-active cathode based on a molecular catalyst and organic dye-sensitized p-type nanostructured NiO^{†‡}

Lin Li,^a Lele Duan,^a Fuyu Wen,^b Can Li,^b Mei Wang,^c Anders Hagfeldt^{cd} and Licheng Sun^{*,ac}



Scheme 1 A PEC device, consisting of a photocathode based on a **P1** sensitized nanostructured NiO film on a FTO conducting glass coated with **Co1**, Pt counter electrode, and an aqueous electrolyte (pH 7 buffer), under an applied potential of -0.4 V vs. Ag/AgCl, for light driven hydrogen generation.

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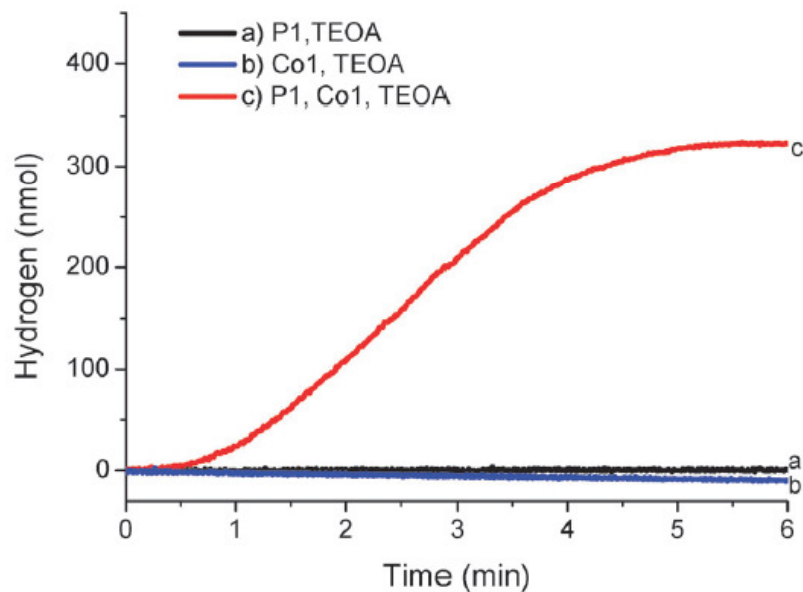


Fig. 1 Photoinduced hydrogen evolution from homogeneous systems containing (a) P1 (5×10^{-5} M), black line; (b) Co1 (2×10^{-4} M), blue line; (c) P1 (5×10^{-5} M) + Co1 (2×10^{-4} M), red line, in 1 mL solution containing 5% TEOA in 1 : 1 MeCN/H₂O, pH 7, detected by a modified Clark electrode, and illuminated by a 500 W xenon lamp through a 400 nm cut off filter.

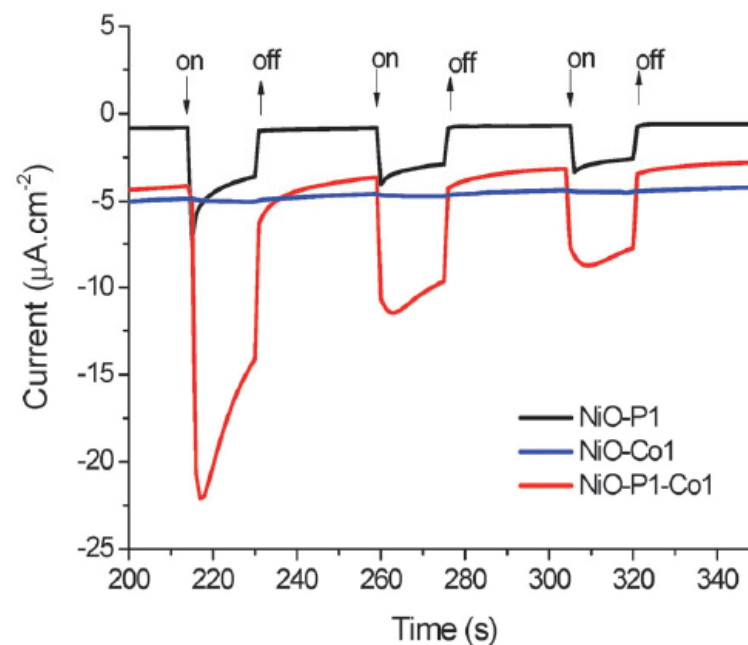


Fig. 2 The transient current responses to on–off cycles of illumination on photocathodes under an applied potential of -0.4 V vs. Ag/AgCl in the PEC with Pt as the counter electrode, operated in a pH 7.0 phosphate buffer solution. The illumination was provided by a light emitting diode, > 400 nm.

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Table 1 Electrochemical properties of P1 and Co1 (V vs. NHE)

	$E(\text{Co}^{\text{II}}/\text{Co}^{\text{I}})$	$E(\text{D}/\text{D}^-)^a$	Reference
Co1	-0.43		33
P1		-0.83	21,22

^a $E(\text{D}/\text{D}^-)$ ground state reduction potential of the dye.

