

Overall Water Splitting Using Visible Light in a Molecular Photoelectrochemical System

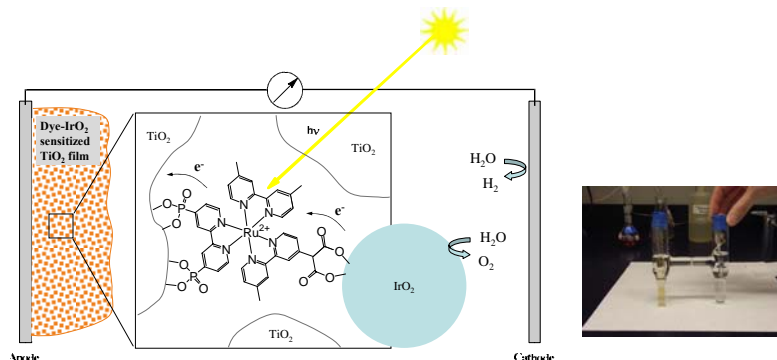
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Visible light water splitting

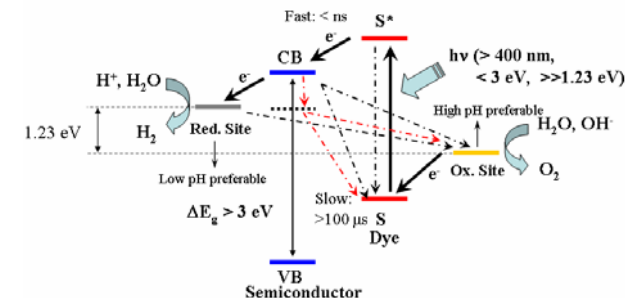
Efficient, overall water splitting with visible light has been described as one of the “holy grails” of chemistry. While overall water splitting has been demonstrated with oxynitride semiconductors, the quantum yield is typically low (< 2%). So far there are no molecular systems (apart from photosynthesis) that can catalyze overall water splitting, even with low quantum efficiency.

One impediment to realizing molecular water splitting systems is the low turnover rate (10^{-3} - 10^{-1} s⁻¹) of known oxygen-evolving catalysts. We have recently found that colloidal IrO₂ has turnover rates in the range of 50 s⁻¹ per surface Ir atom, which can be competitive with back electron transfer rates in some molecular donor-acceptor systems.

A water-splitting dye sensitized solar cell

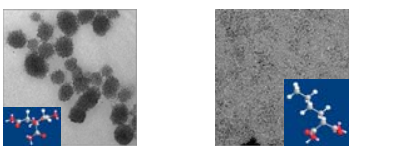


Energetic & kinetic considerations



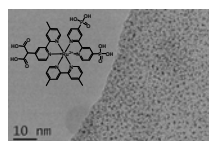
The absorbed light energy must generate excited electrons with sufficiently negative potential to reduce water to hydrogen, and “holes” with sufficiently positive potential to oxidize water to oxygen. Forward rates must be competitive with backward rates.

Colloidal IrO₂ water oxidation catalysts



Citrate, Na⁺ - IrO₂ Butylmalonic acid, Na⁺ - IrO₂

Previously, citrate has been used to stabilize colloidal IrO₂, but it causes the colloid to aggregate into larger particles, probably due to the presence of three carboxylates per molecule. We have found that stabilizers having malonate or succinate functionality provide well-dispersed, small (~1-2 nm) particles of IrO₂.

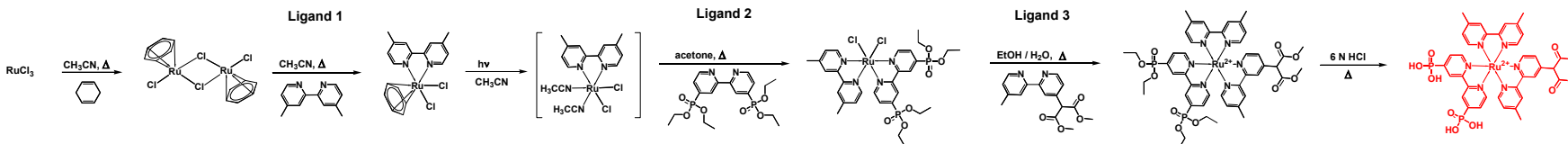


Dye molecules cannot displace the stabilizer to adsorb onto IrO₂.

Therefore, we use a malonate-functionalized dye as the stabilizer.

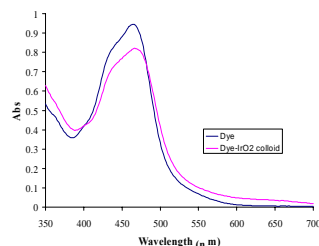
Heteroleptic Dye-Stabilized IrO₂

Synthesis of the heteroleptic dye

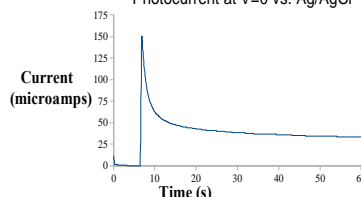


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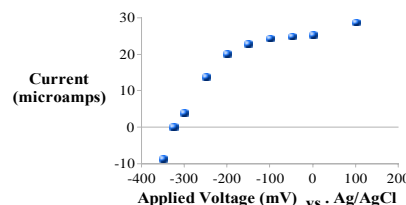
Visible Absorbance by Dye and Dye-IrO₂



Photocurrent at V=0 vs. Ag/AgCl



The photocurrent is generated by oxidation of water at IrO₂. An electrode with only the TiO₂ film generates a much smaller photocurrent (2-4 μA).



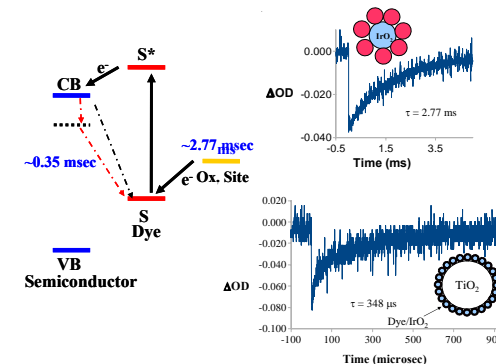
The effective open circuit voltage (V_{oc}) is obtained by adding the formal potential of the oxygen/water couple (vs. Ag⁺/AgCl) at pH 5.75 to the current onset potential.

$$V_{oc} = 555 \text{ mV} + 325 \text{ mV} = 880 \text{ mV}$$

Gas chromatography confirms that O₂ and H₂ are produced at the anode and cathode, respectively

External quantum efficiency (EQE) = 0.8%

The low EQE (electrons produced per photons absorbed) is due to the unfavorable electron transfer kinetics of the system (see panel at right).



The electron transfer kinetics are currently unfavorable for the overall reaction. The forward electron transfer rate from IrO₂ to the dye is an order of magnitude slower than the back transfer of electrons from the TiO₂.

Future efforts will focus on improving this kinetic branching ratio by varying the distance between the dye molecules and other components, by making IrO₂ clusters capped by fewer dye molecules, by exploring the use of porphyrin-based dyes, and by searching for more active oxygen evolution catalysts.