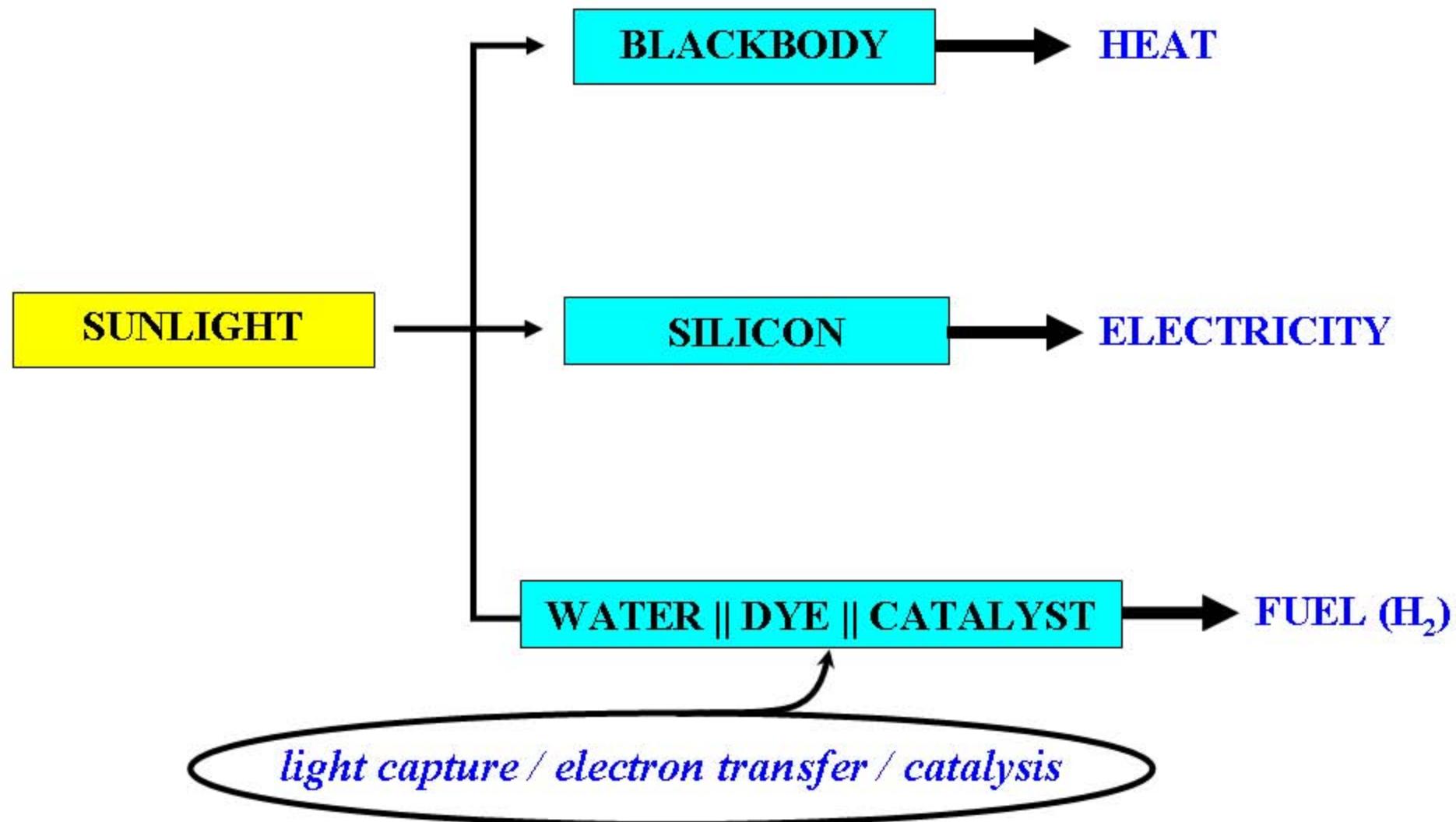


Solar Photochemistry
Harry Gray
NRG 0.1 9 November 2007

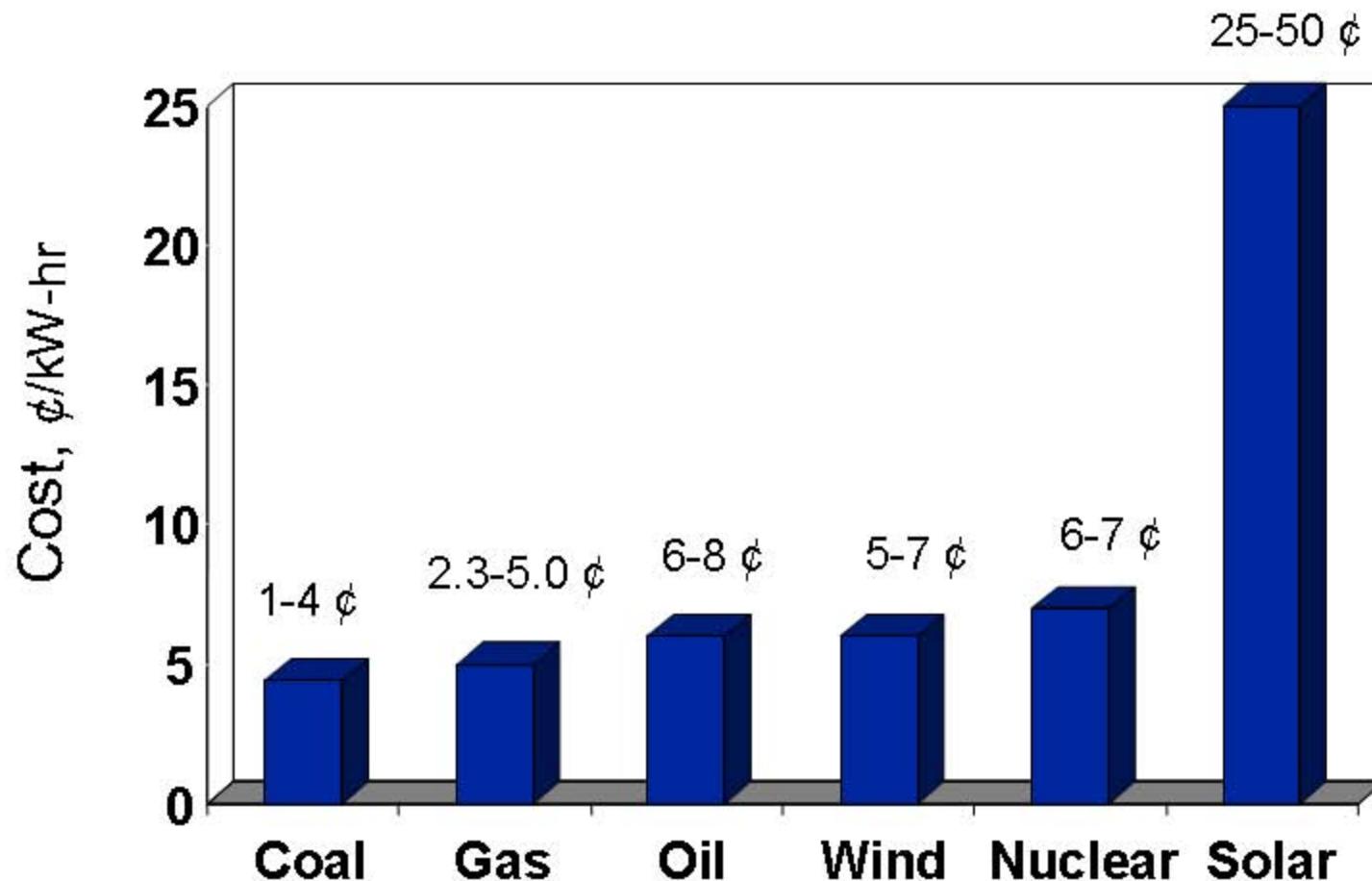


Solar Energy Conversion



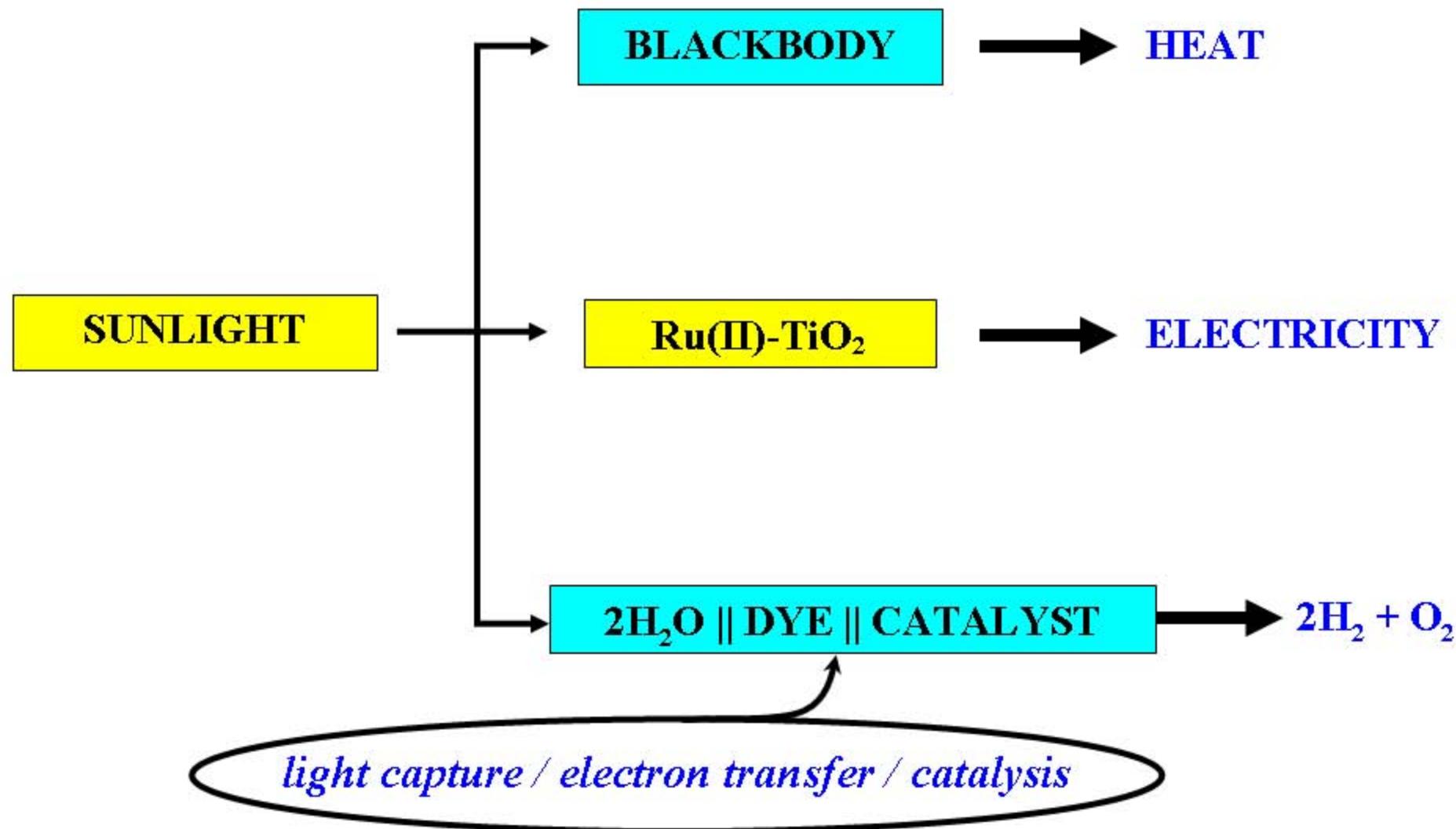
Production Cost of Electricity

United States, 2002



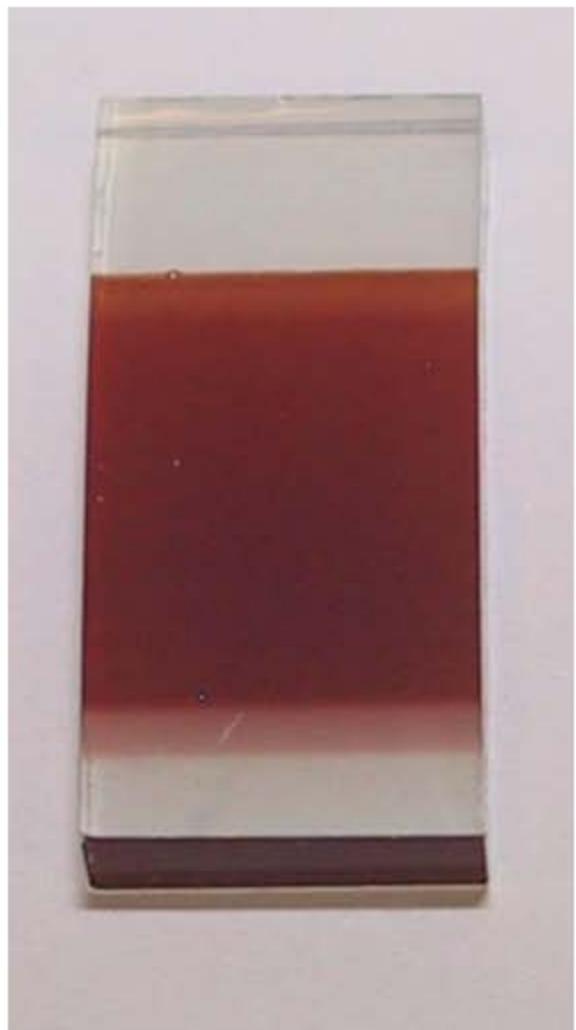
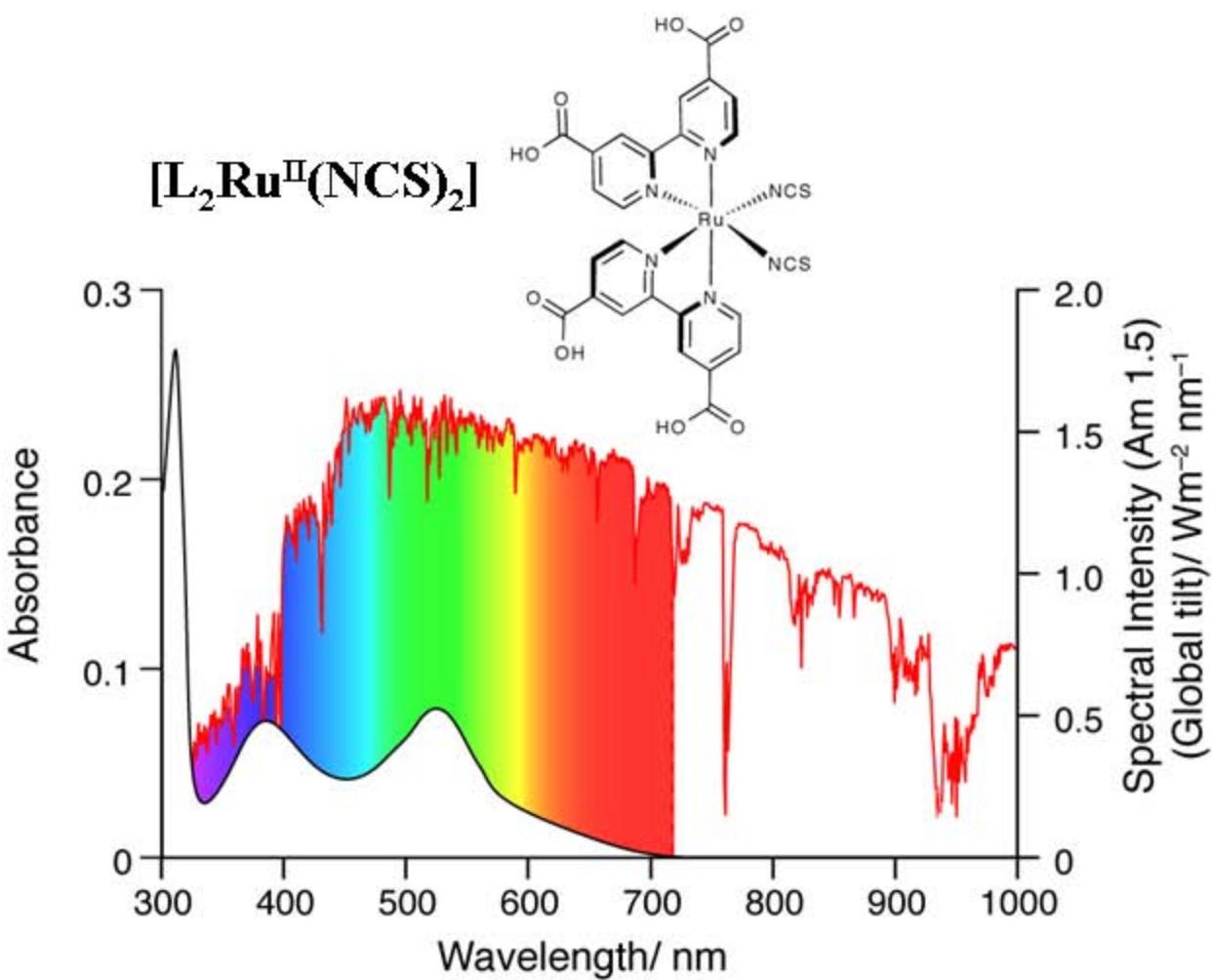
Source: Nate Lewis

Solar Energy Conversion



Solar Energy Conversion

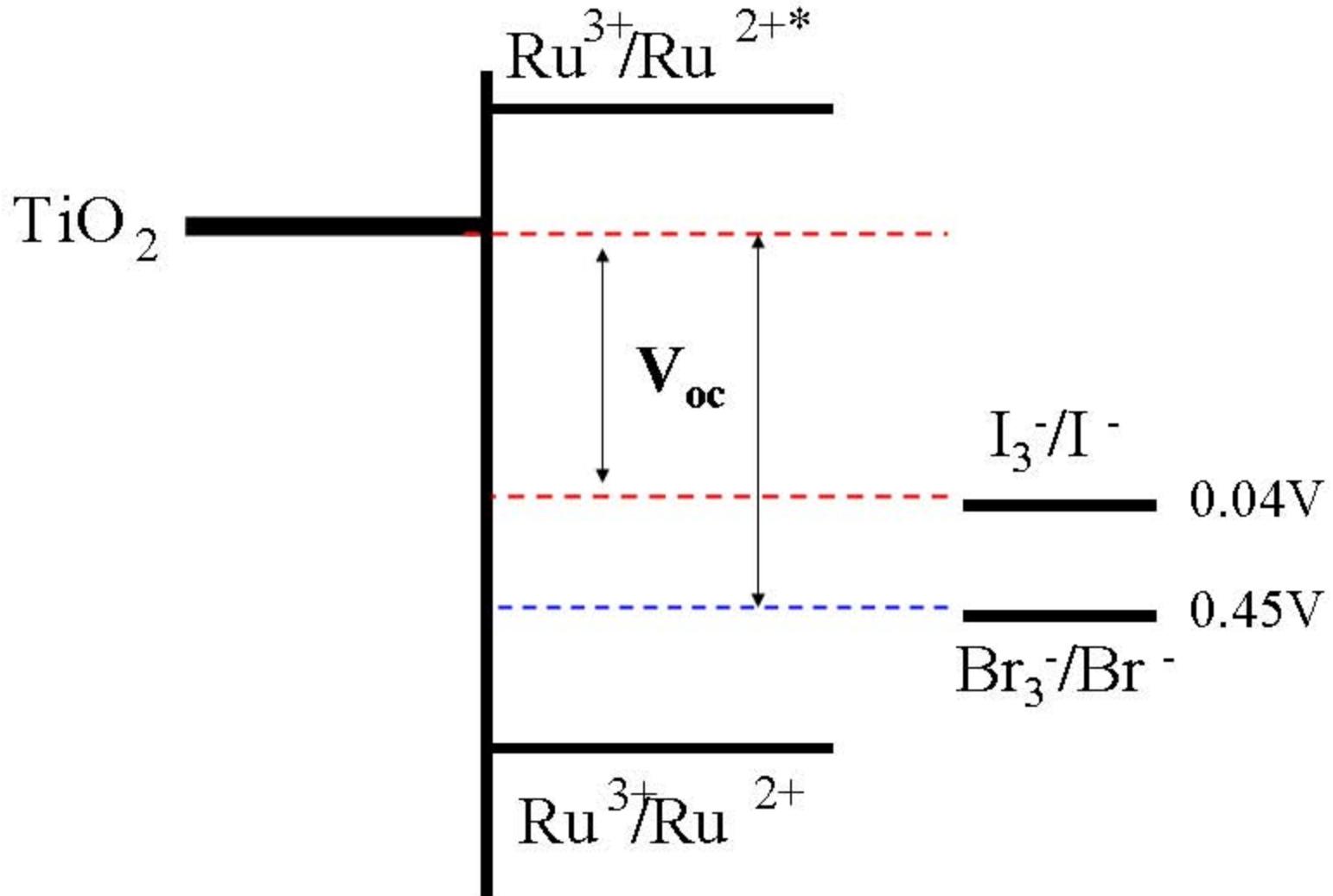
SUNLIGHT → $Ru^{II}-TiO_2$ → ELECTRICITY



Dye-Sensitized Solar Cells



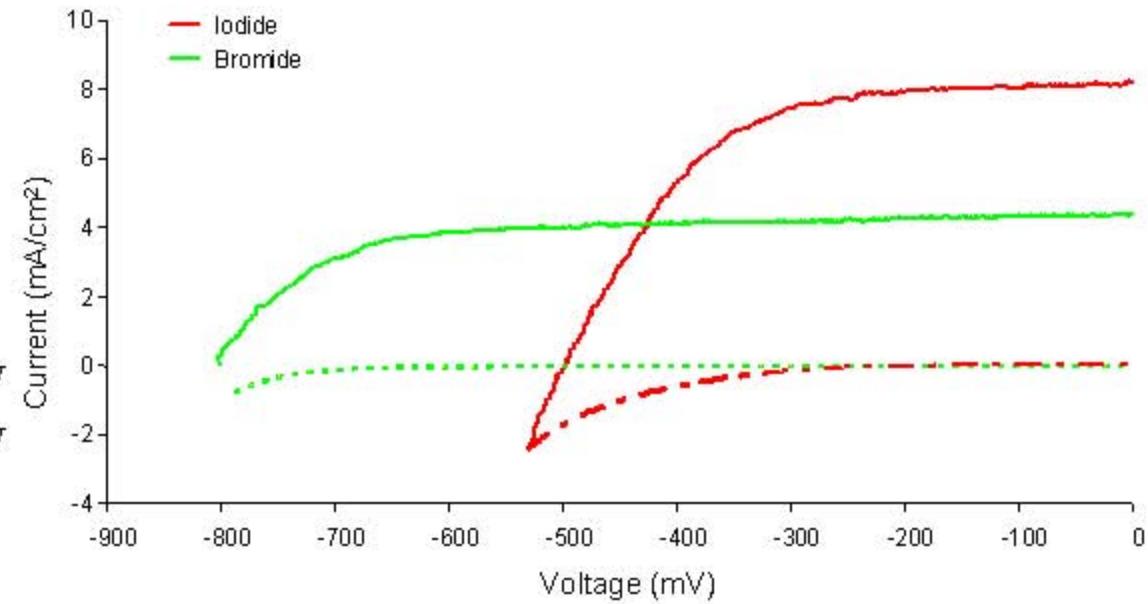
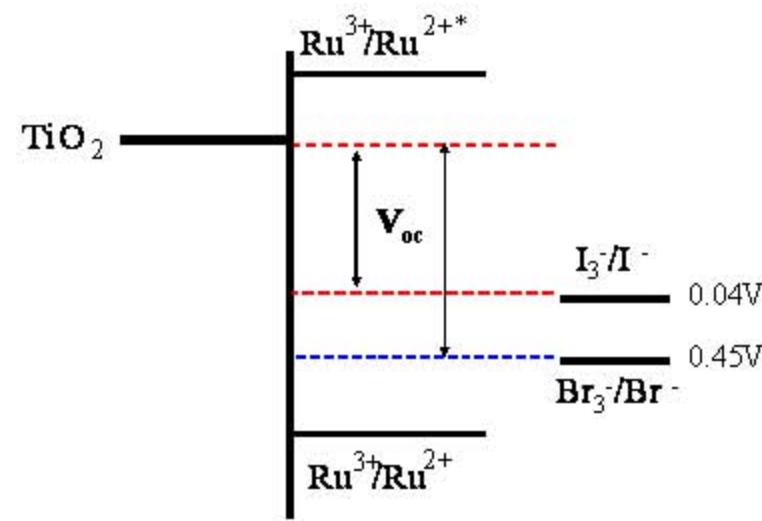
Increase V_{oc}



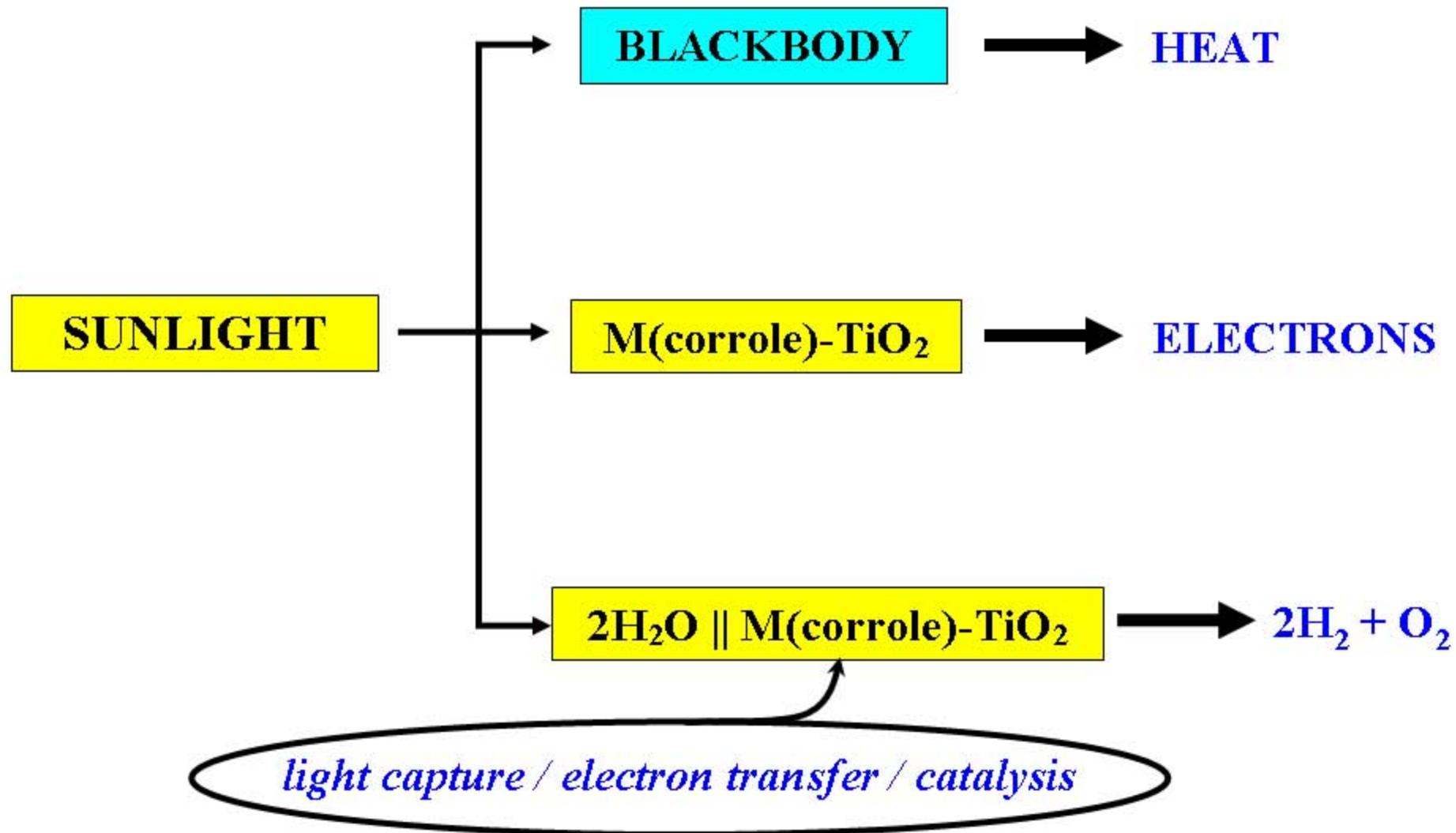
Power Generation

$L_2Ru^{II}(CN)_2$ - TiO_2 Solar Cell

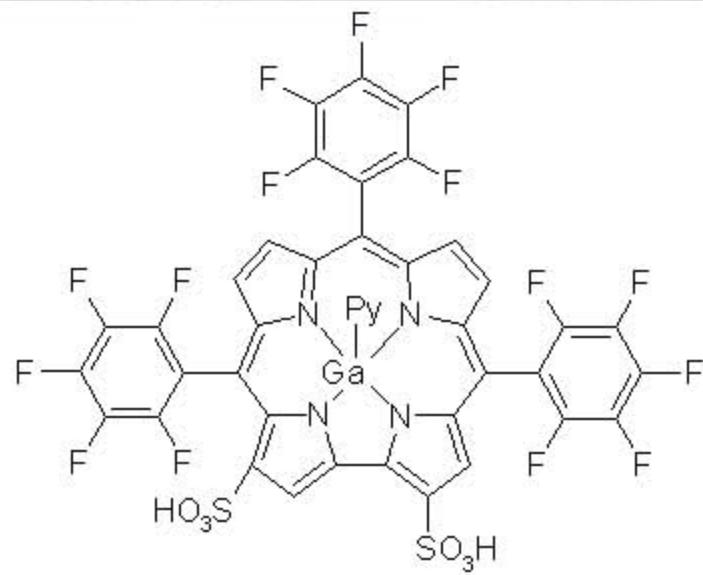
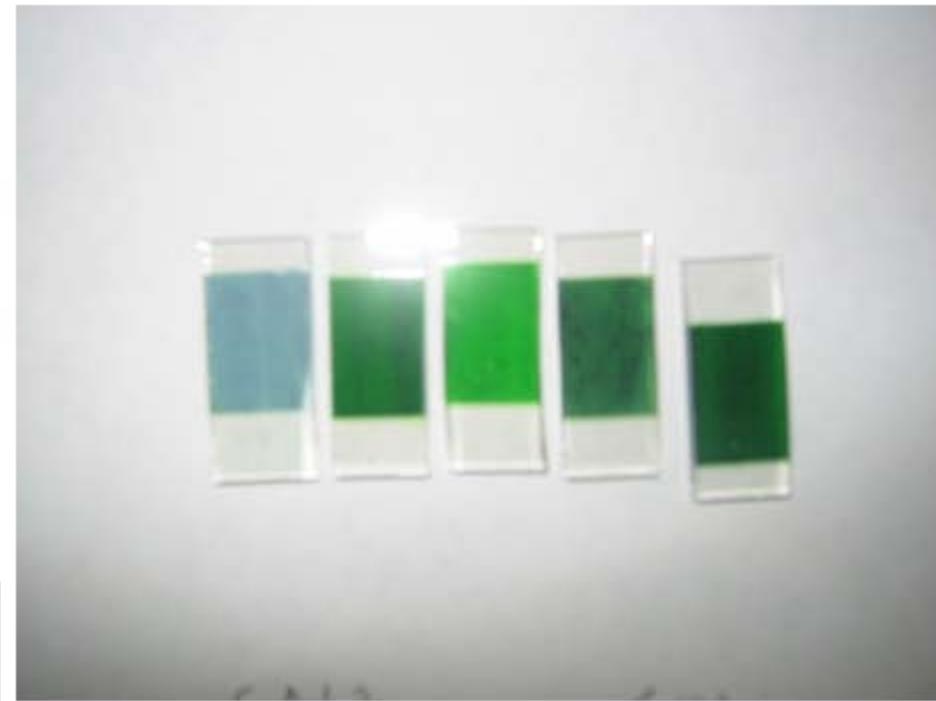
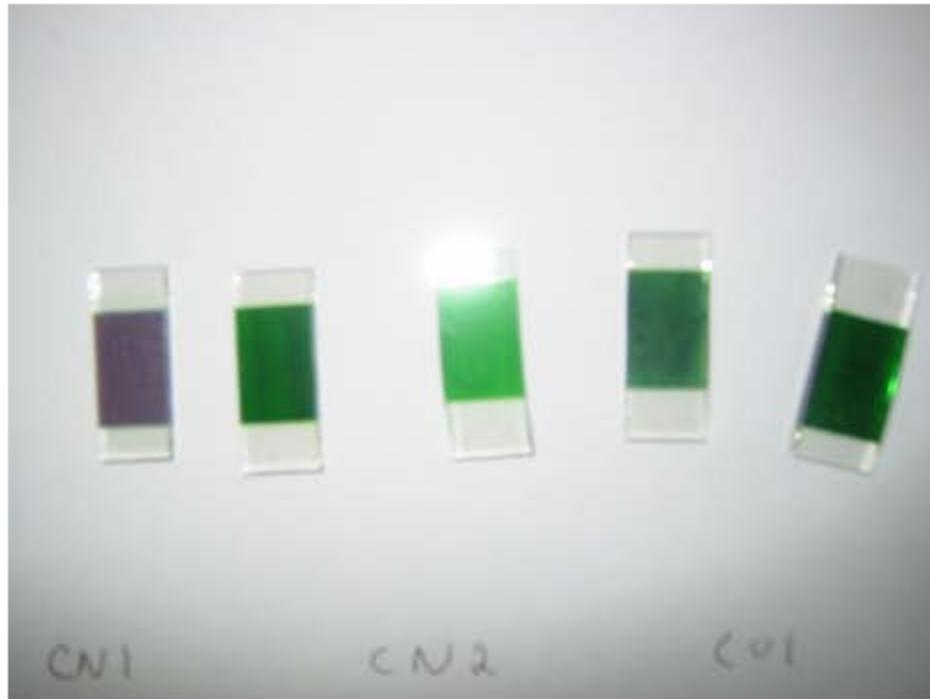
Increase V_{oc}



SOLAR ENERGY CONVERSION

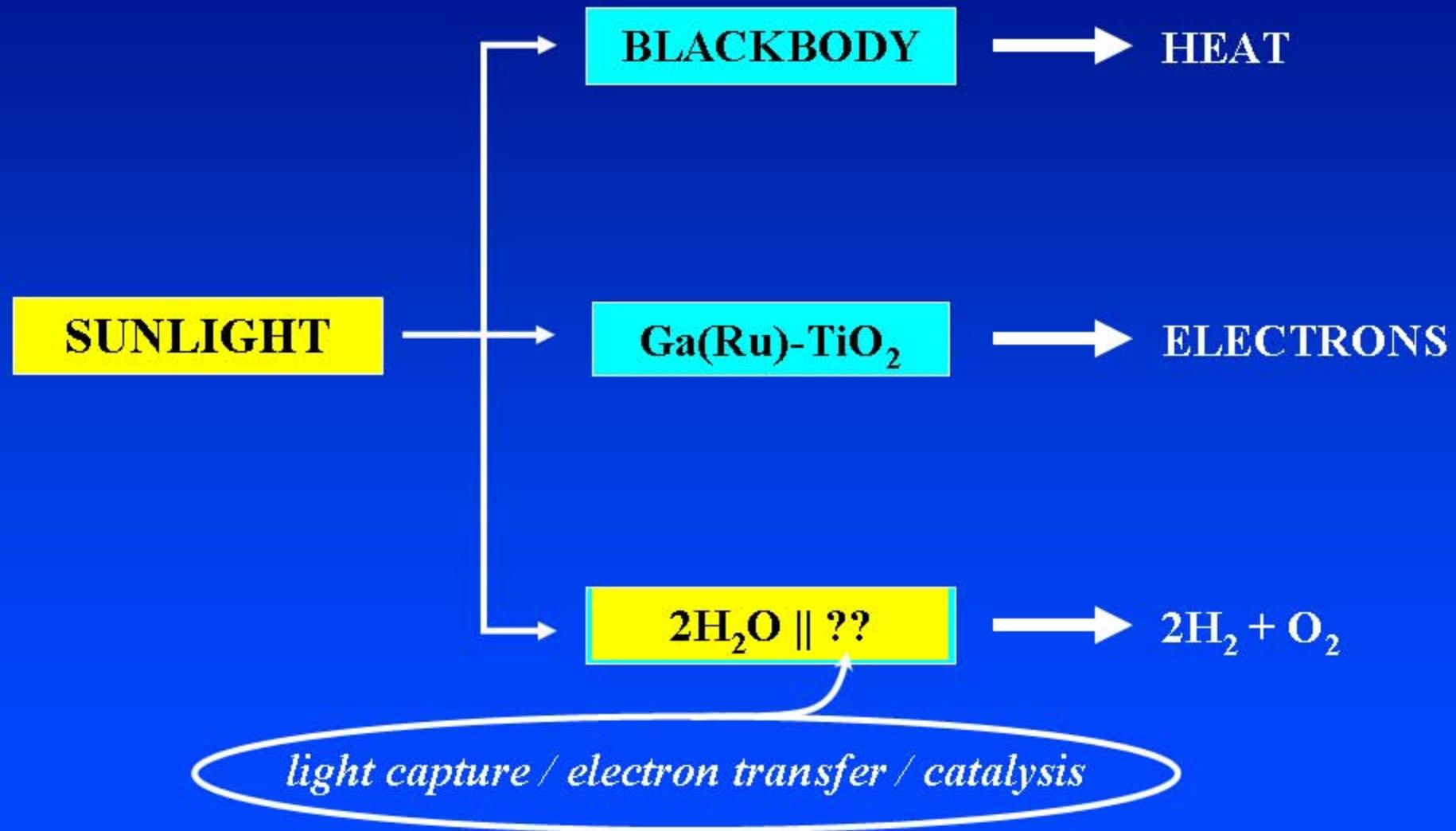


Gallium(III) Solar Paint

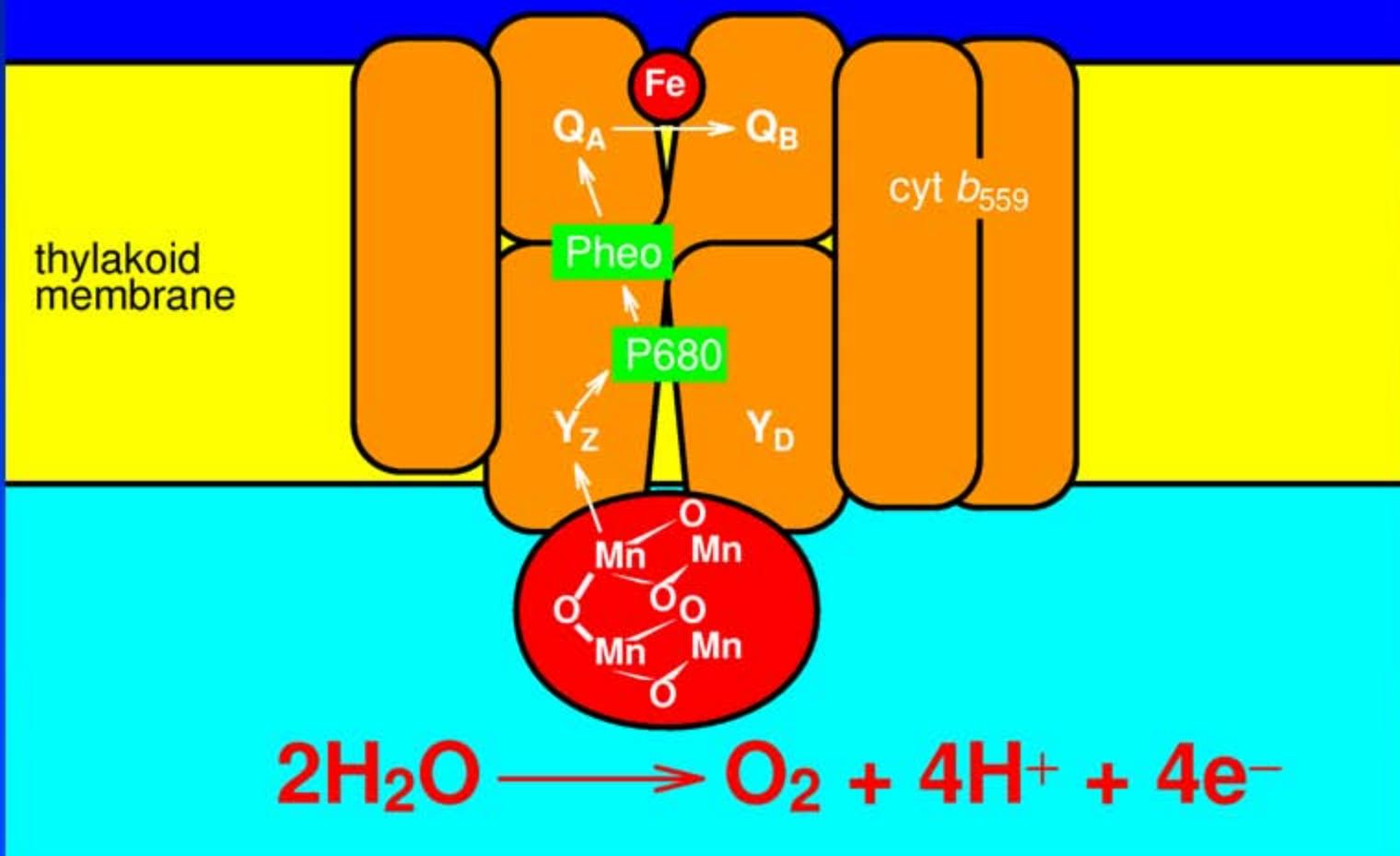


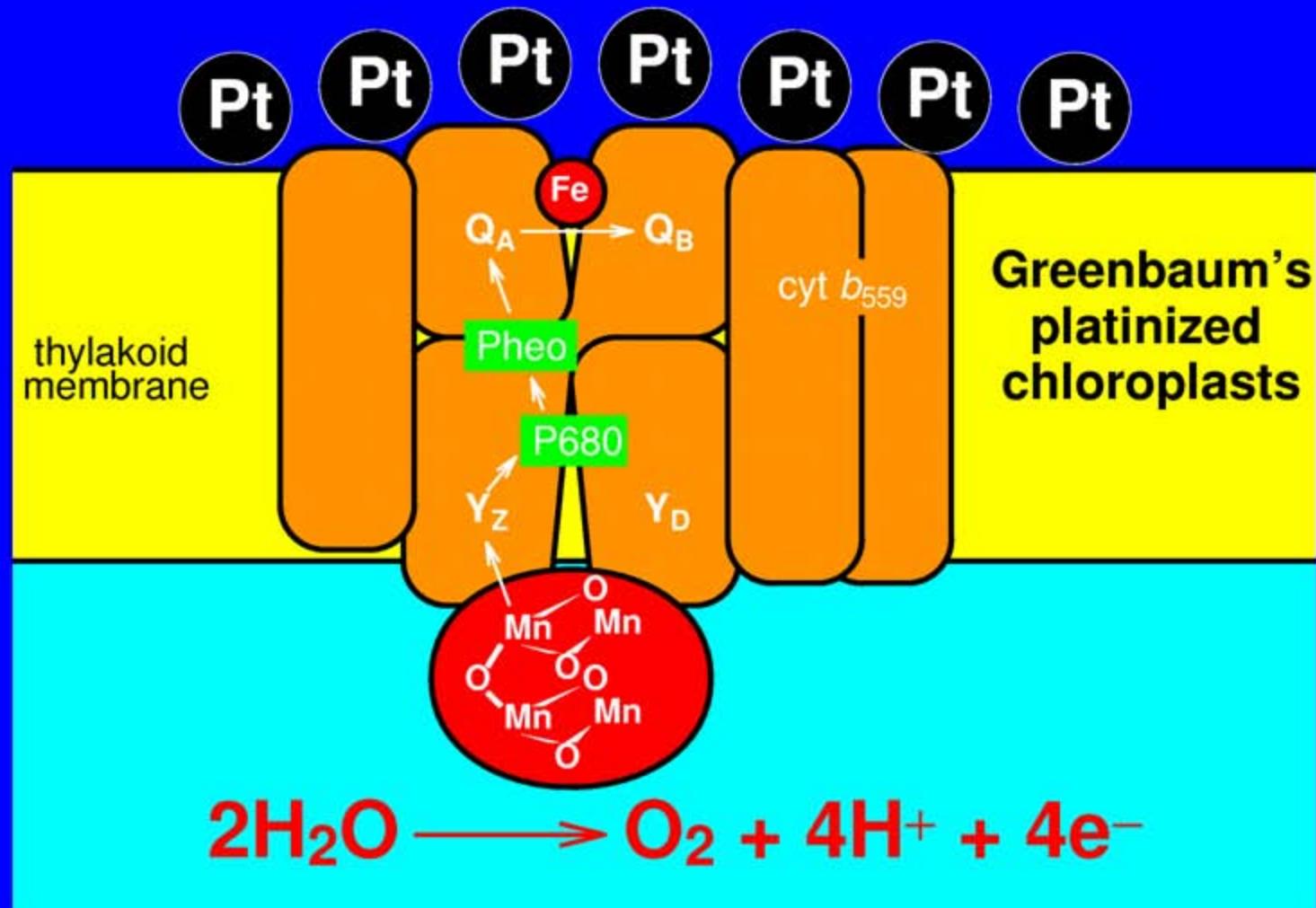
Ga(III) corrole

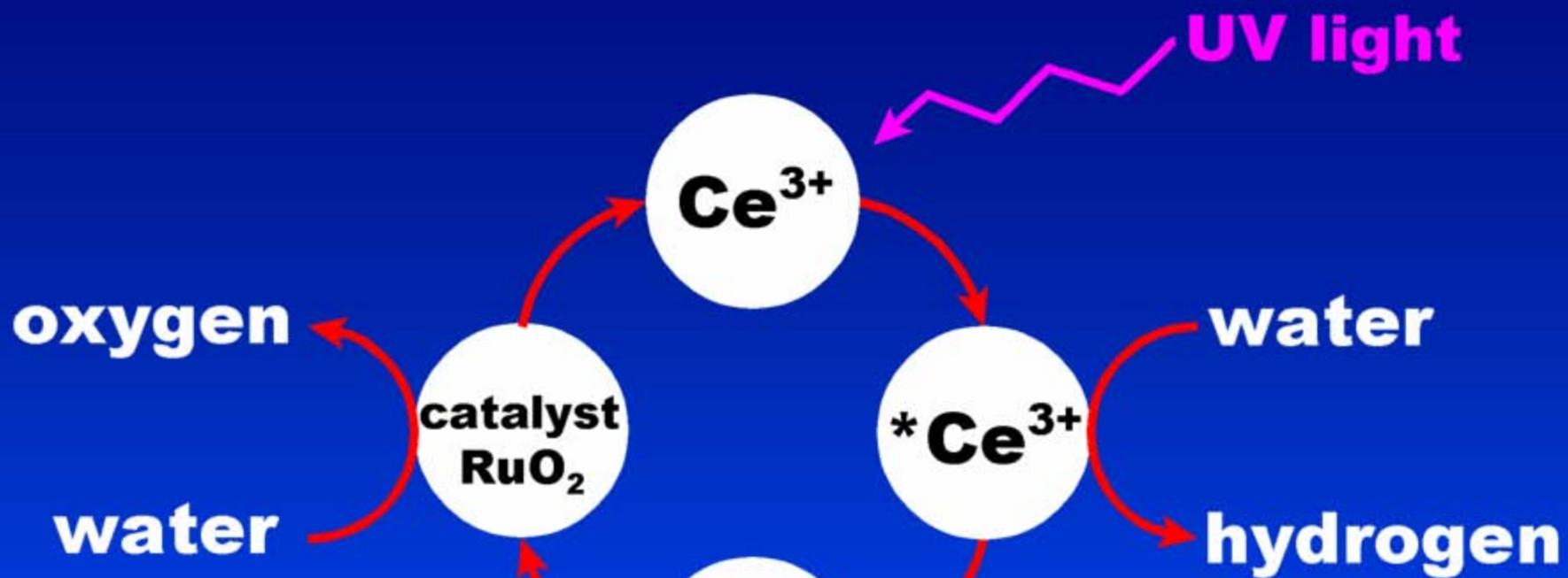
SOLAR ENERGY CONVERSION

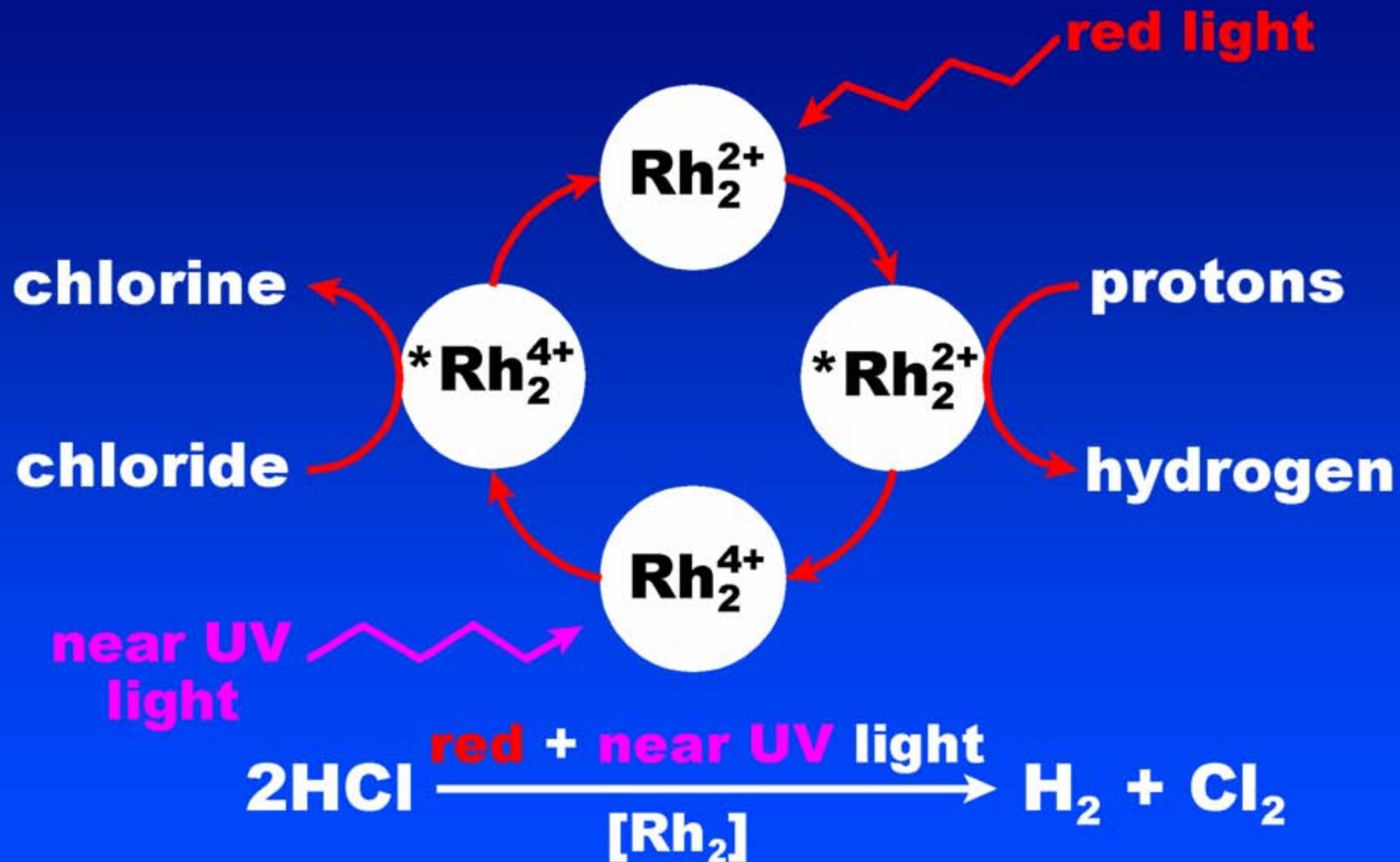


Photosystem II Oxygen-Evolving Complex









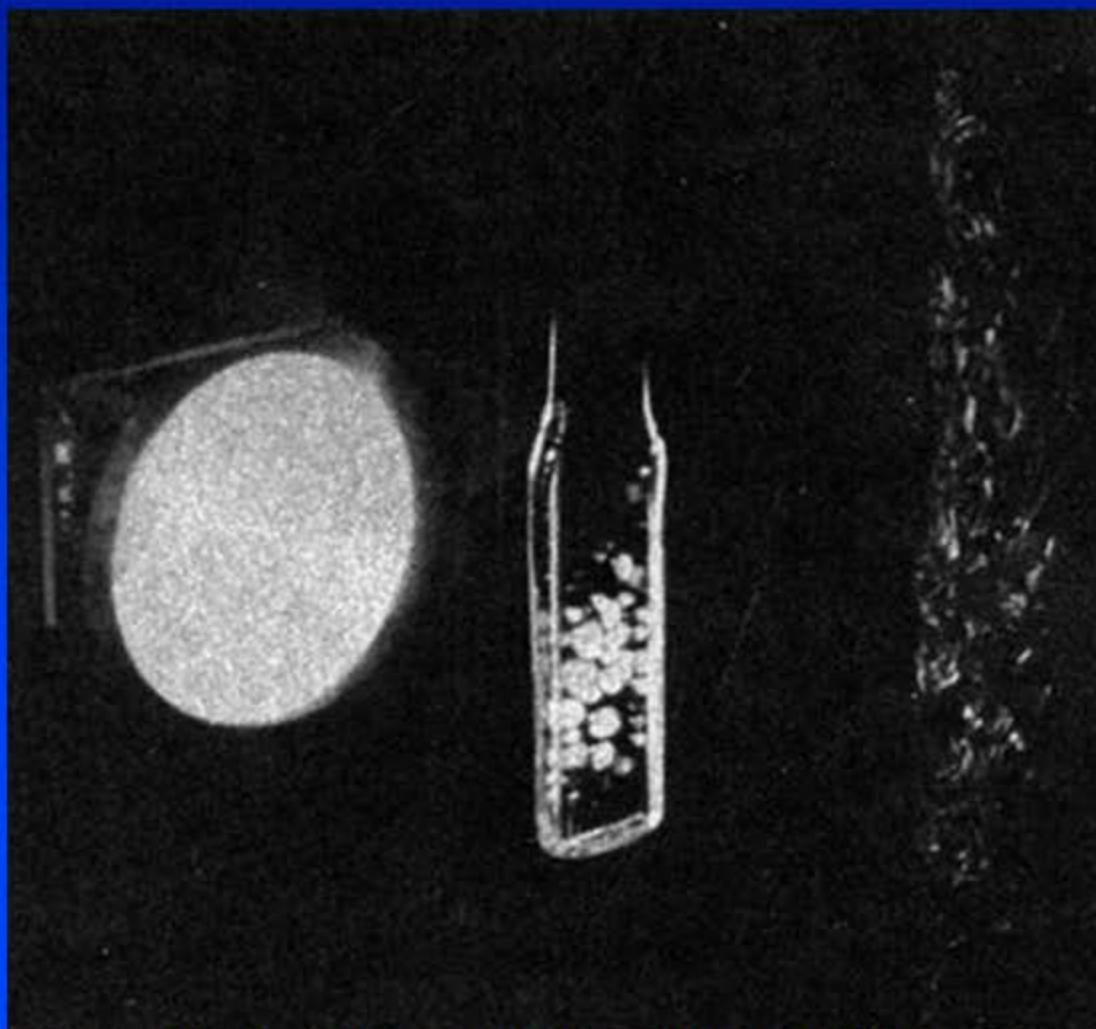
Solar Energy Storage. Production of Hydrogen by 546-nm Irradiation of a Dinuclear Rhodium(I) Complex in Acidic Aqueous Solution

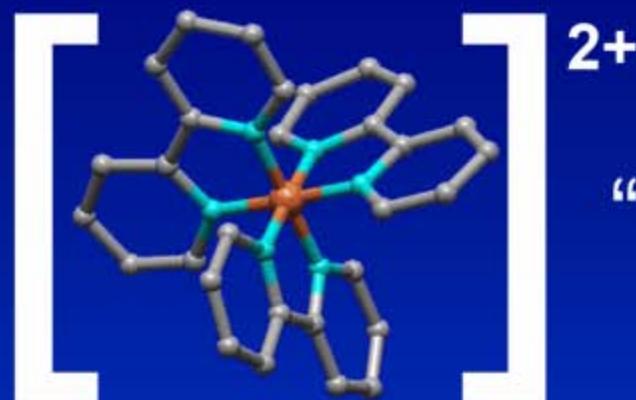
Journal of the American Chemical Society / 99:16 / August 3, 1977

Kent R. Mann,⁷ Nathan S. Lewis, Vincent M. Miskowski
David K. Erwin, George S. Hammond,⁸ Harry B. Gray*

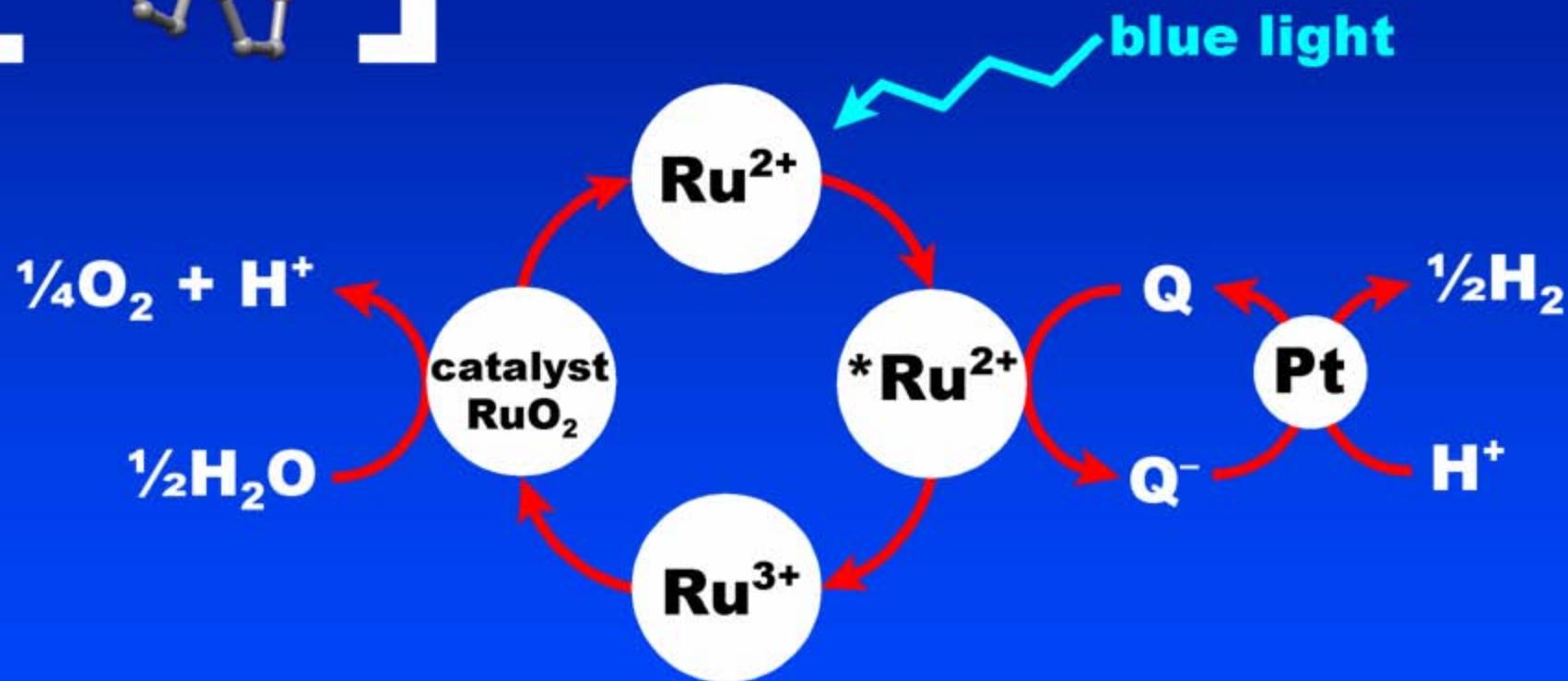
Contribution No. 5587 from the
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

Received May 9, 1977

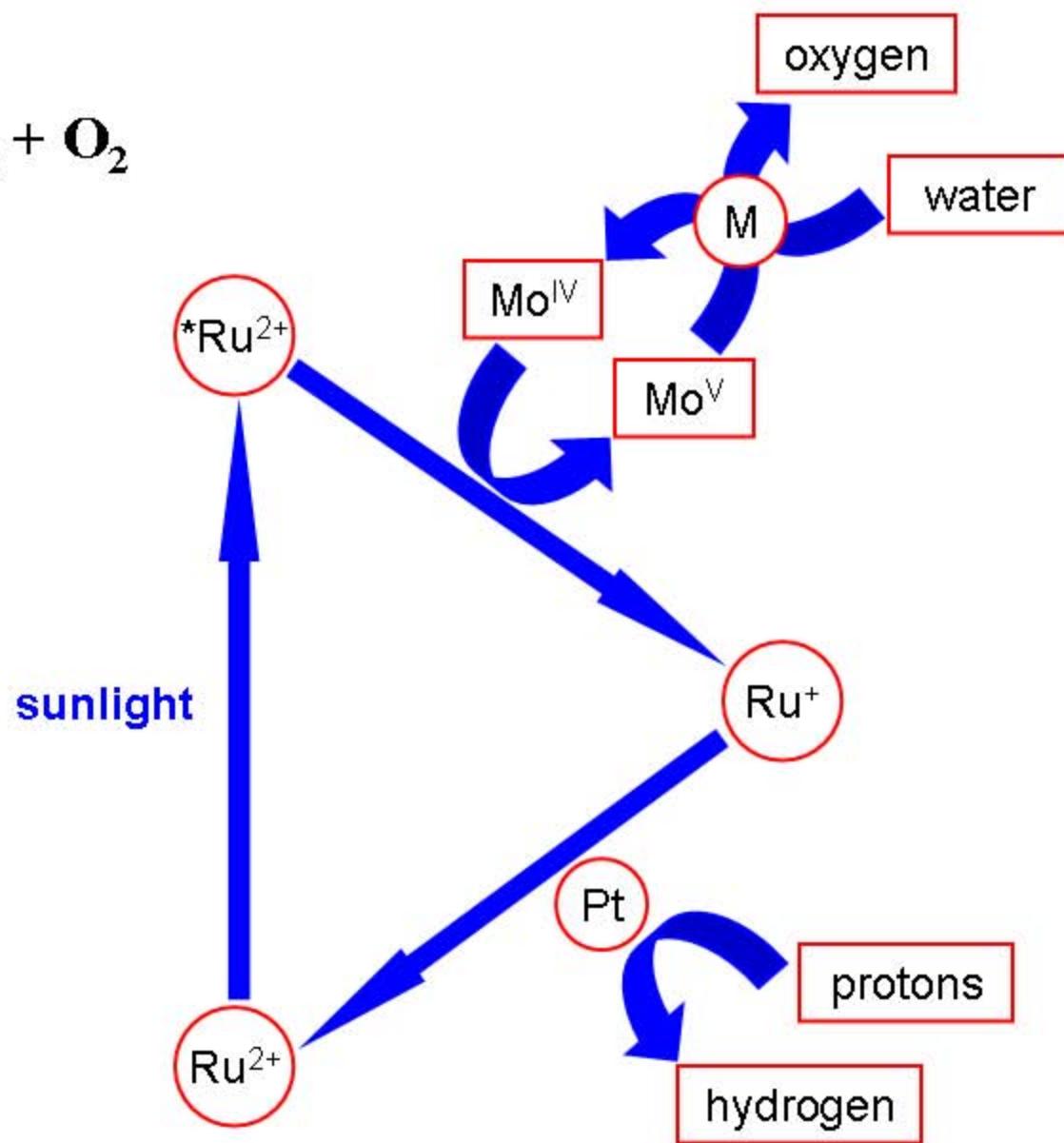




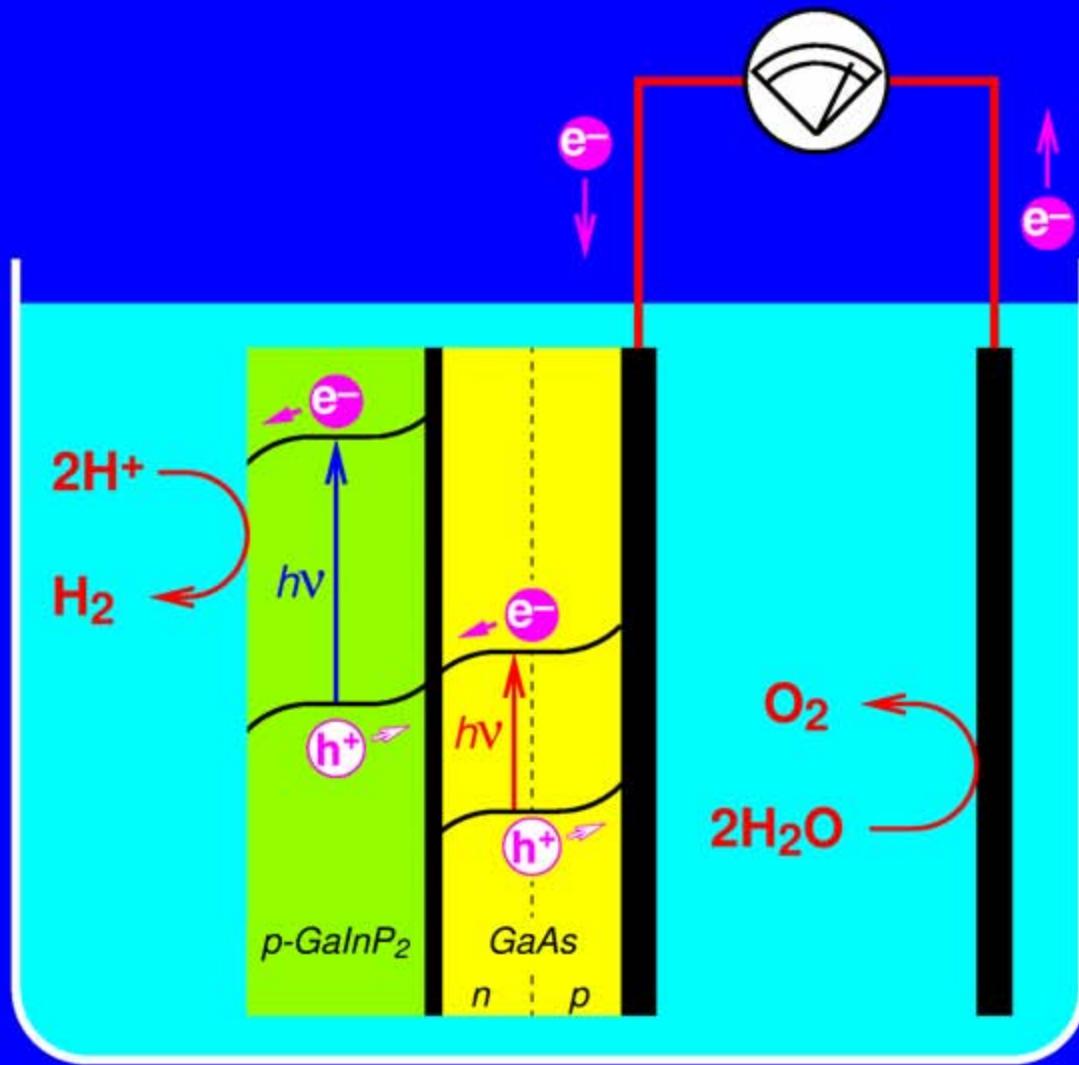
“Ru-bpy”



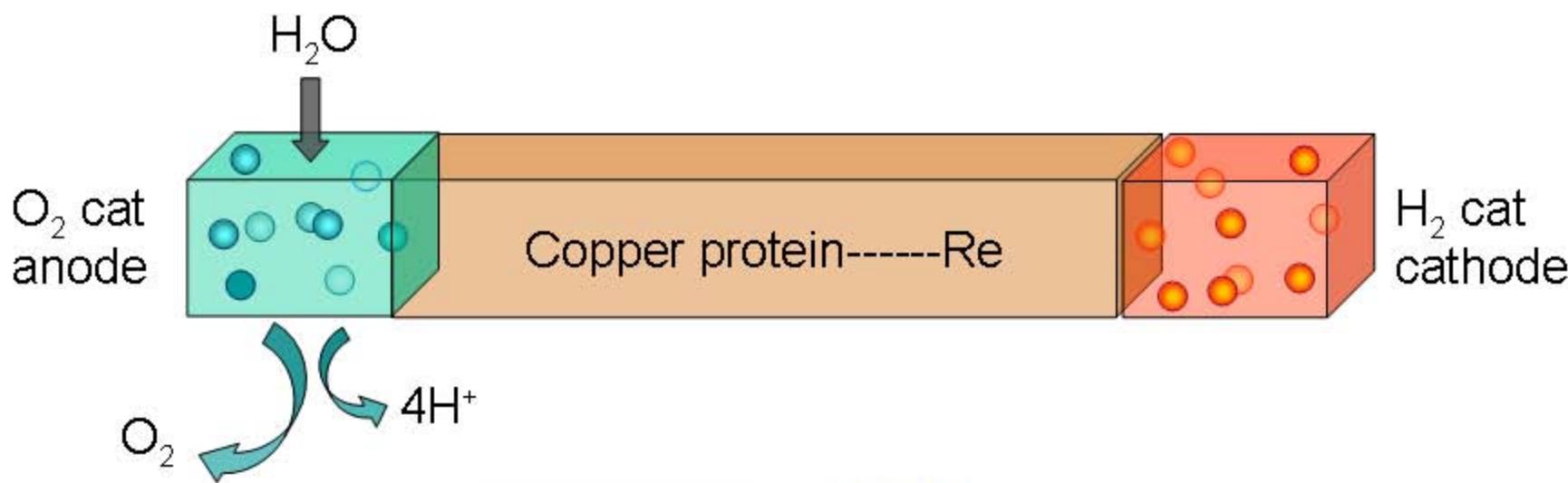
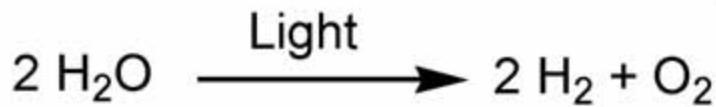
Solar Fuel



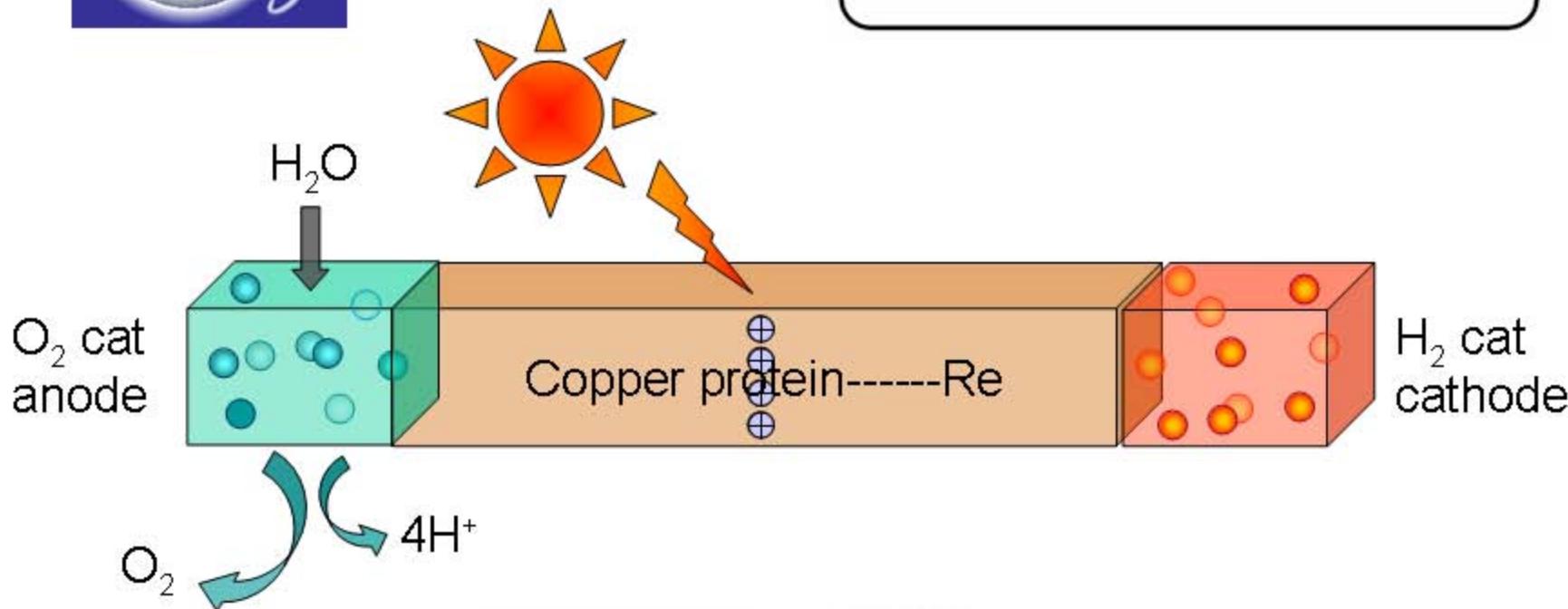
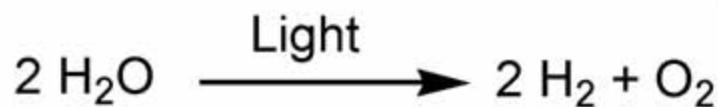
NREL WATER-SPLITTING SOLAR CELL



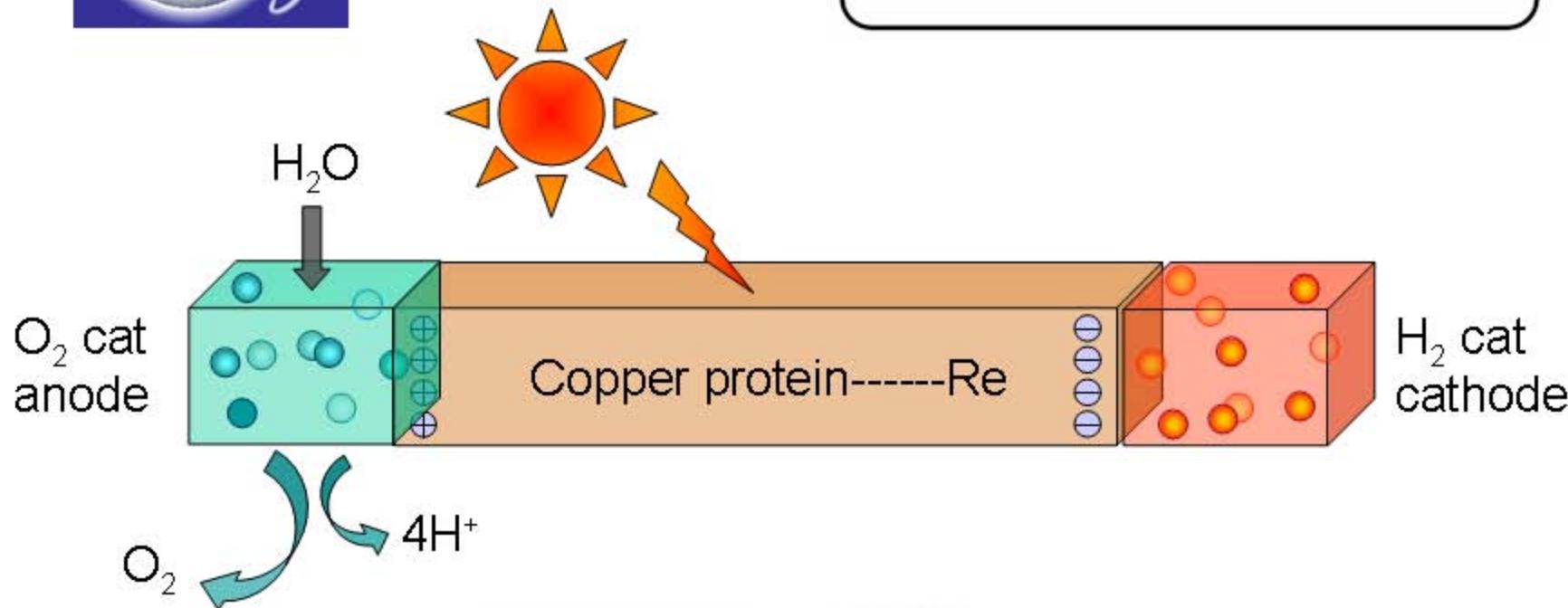
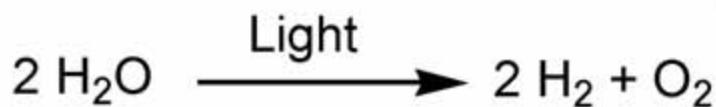
Powering the Planet



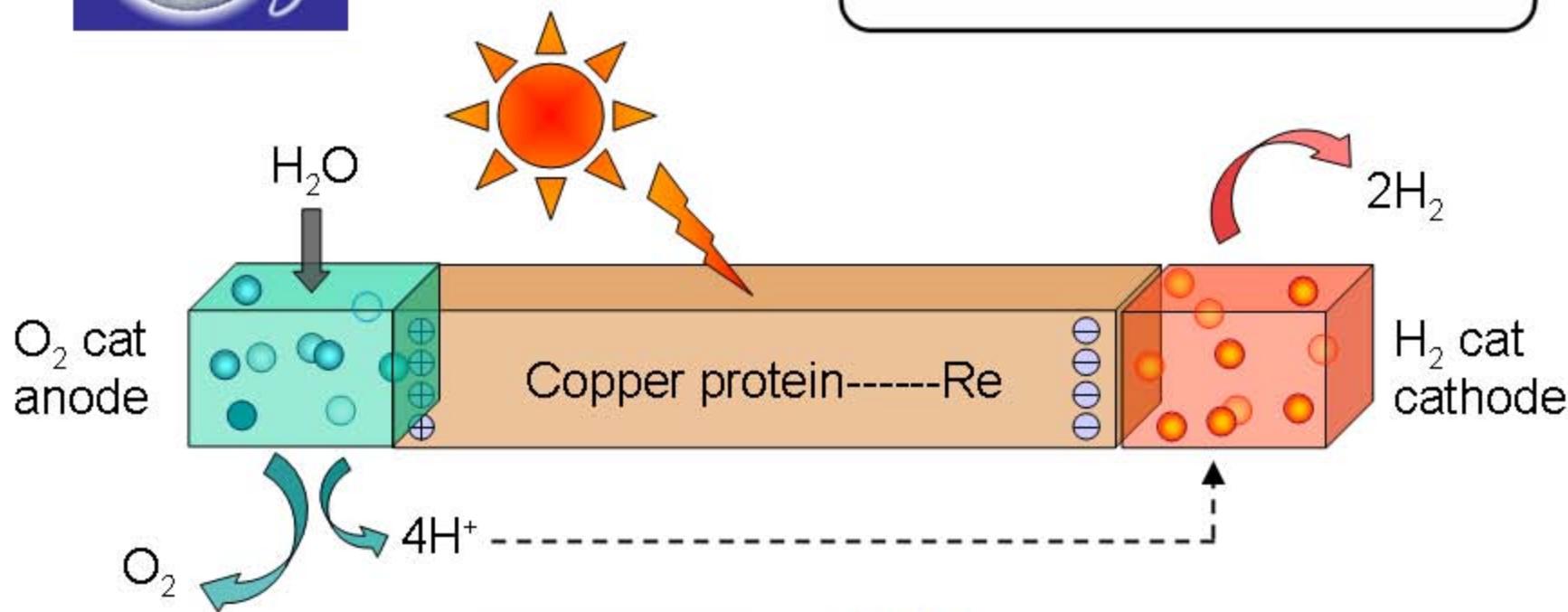
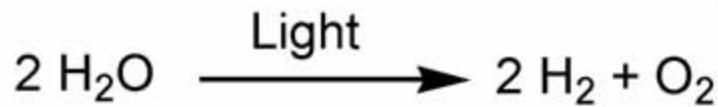
Powering the Planet



Powering the Planet



Powering the Planet



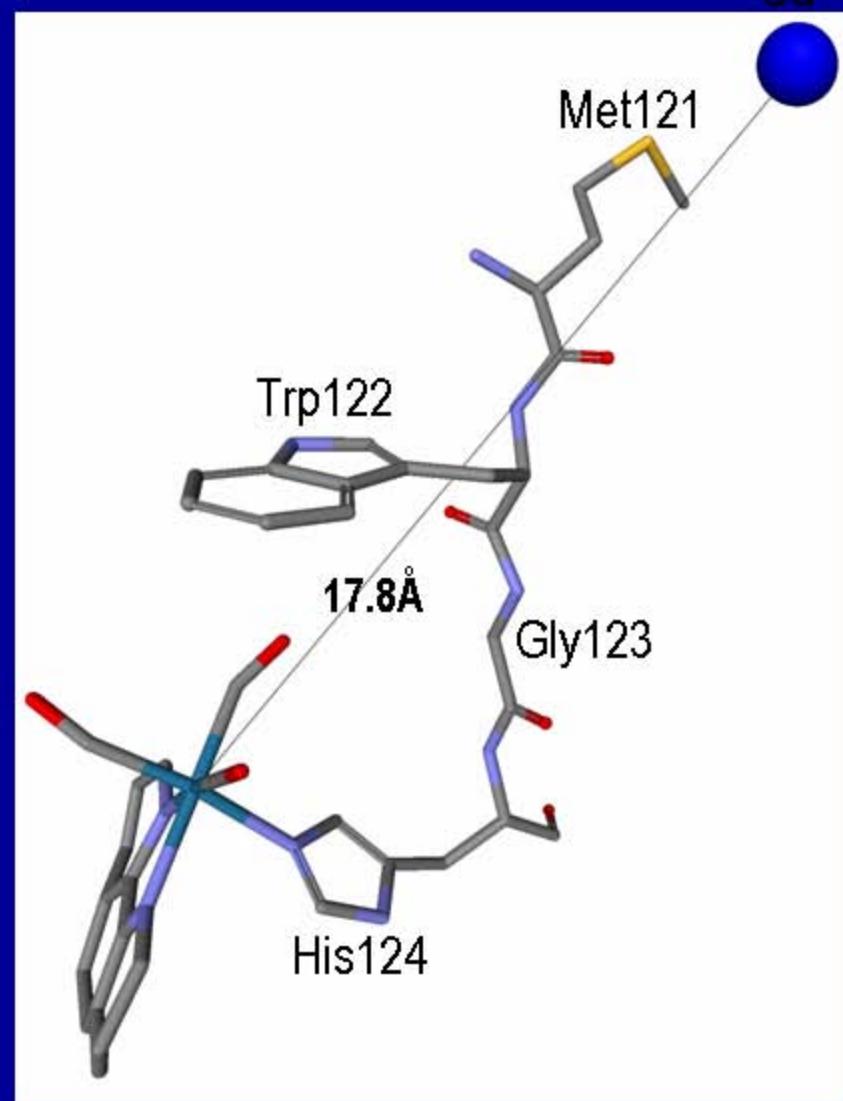
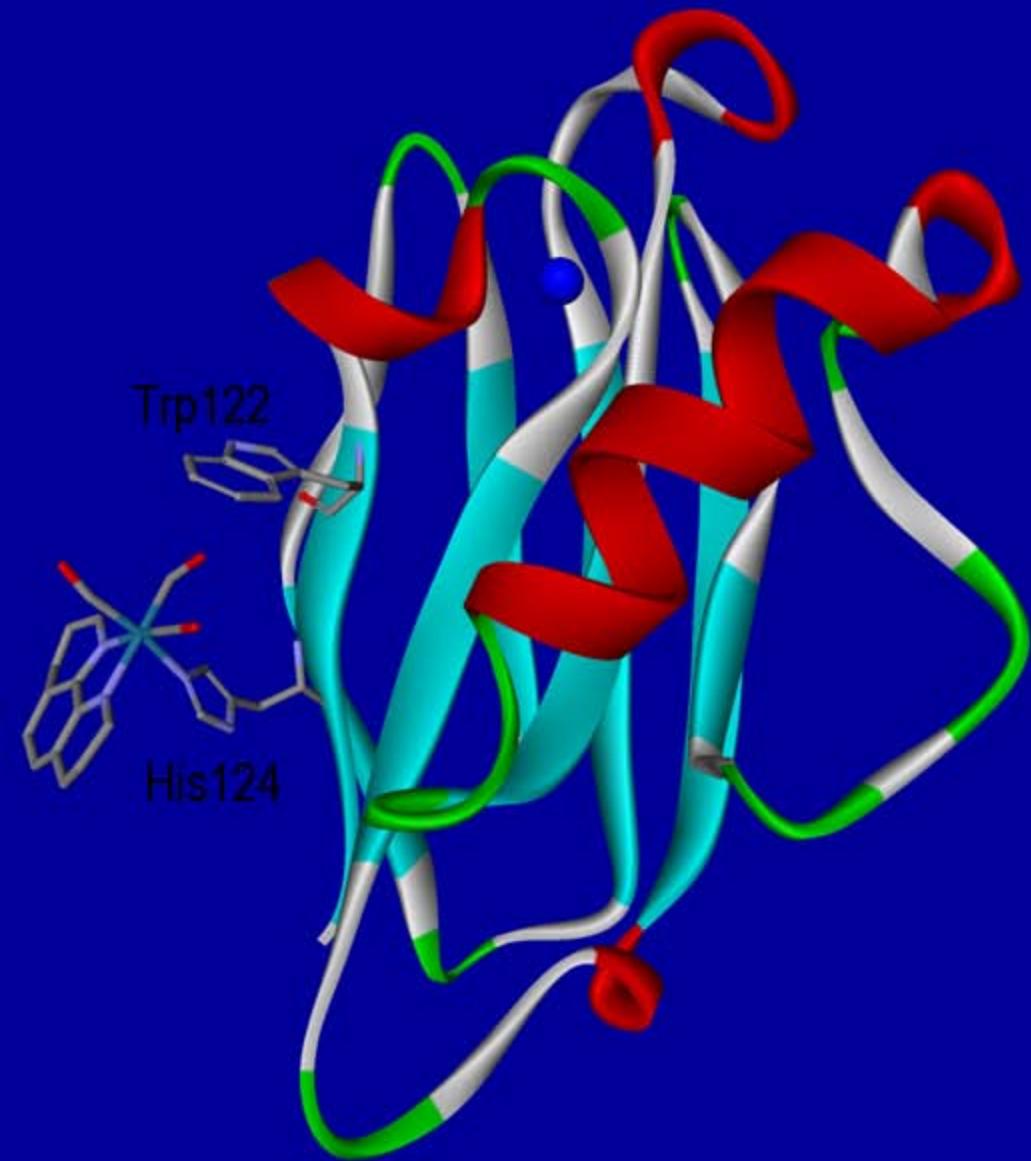


"*E. coli* synthesized"
Pseudomonas aeruginosa azurin

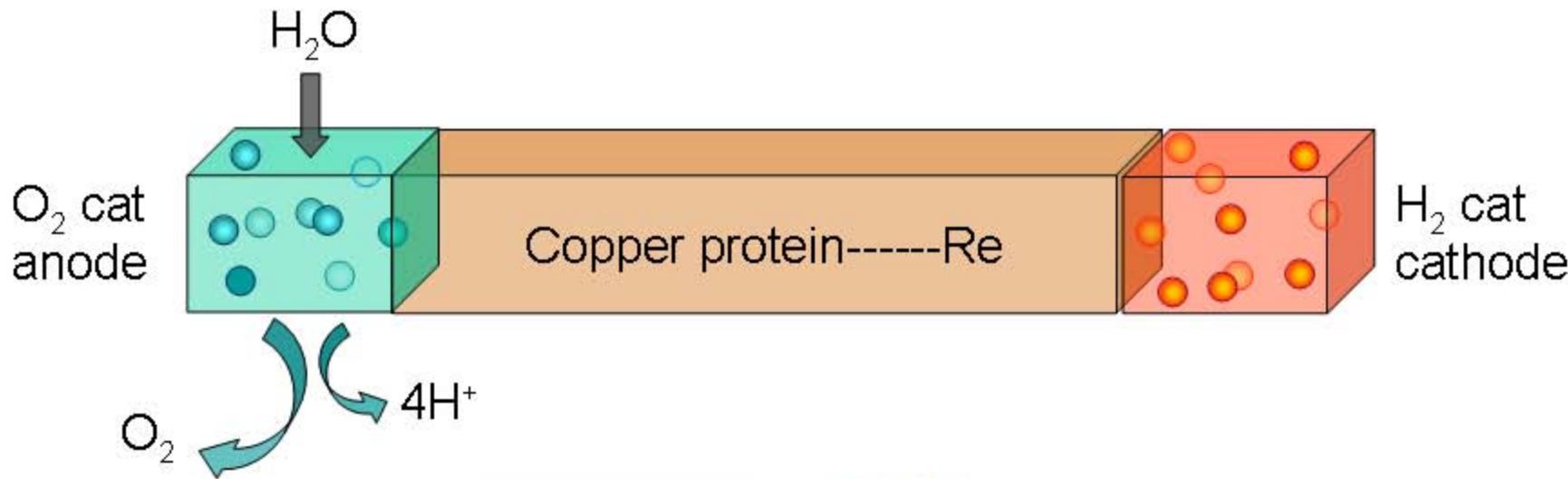
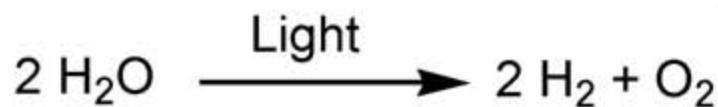


Jack Richards

Re(H124)Az(W122)Cu(II)

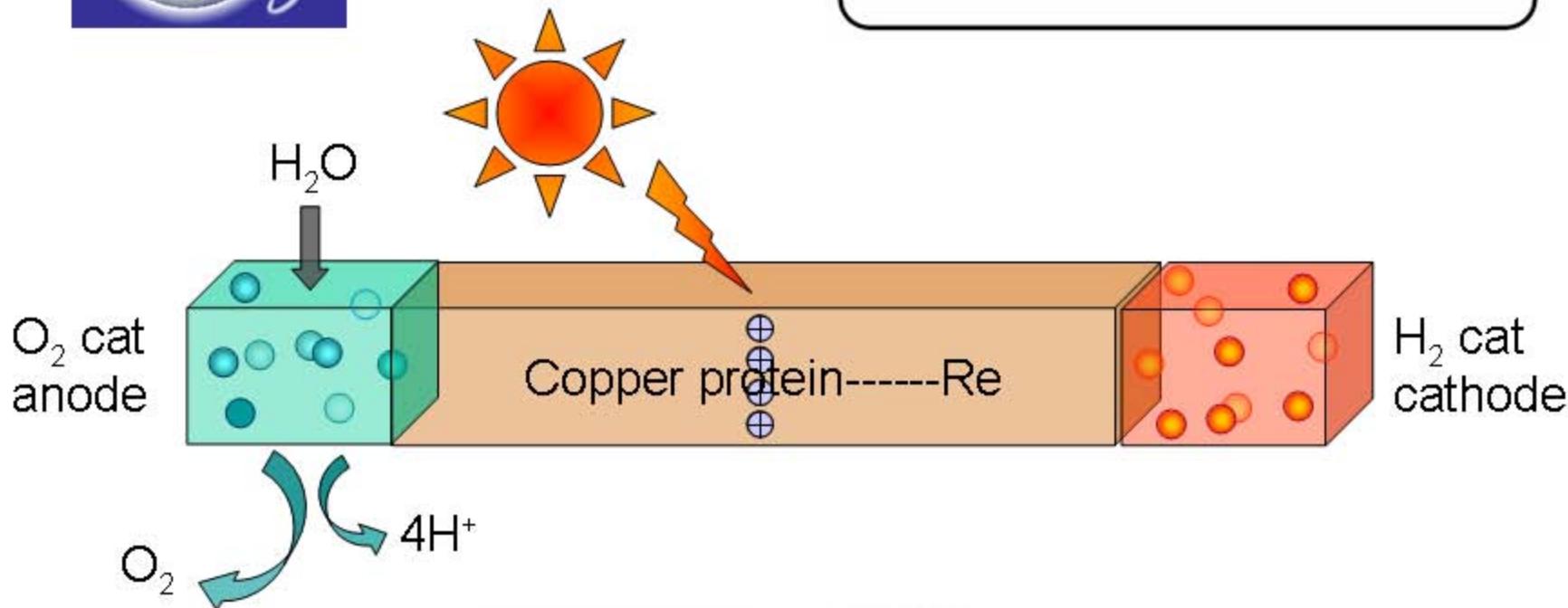
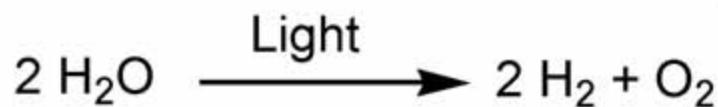


Powering the Planet



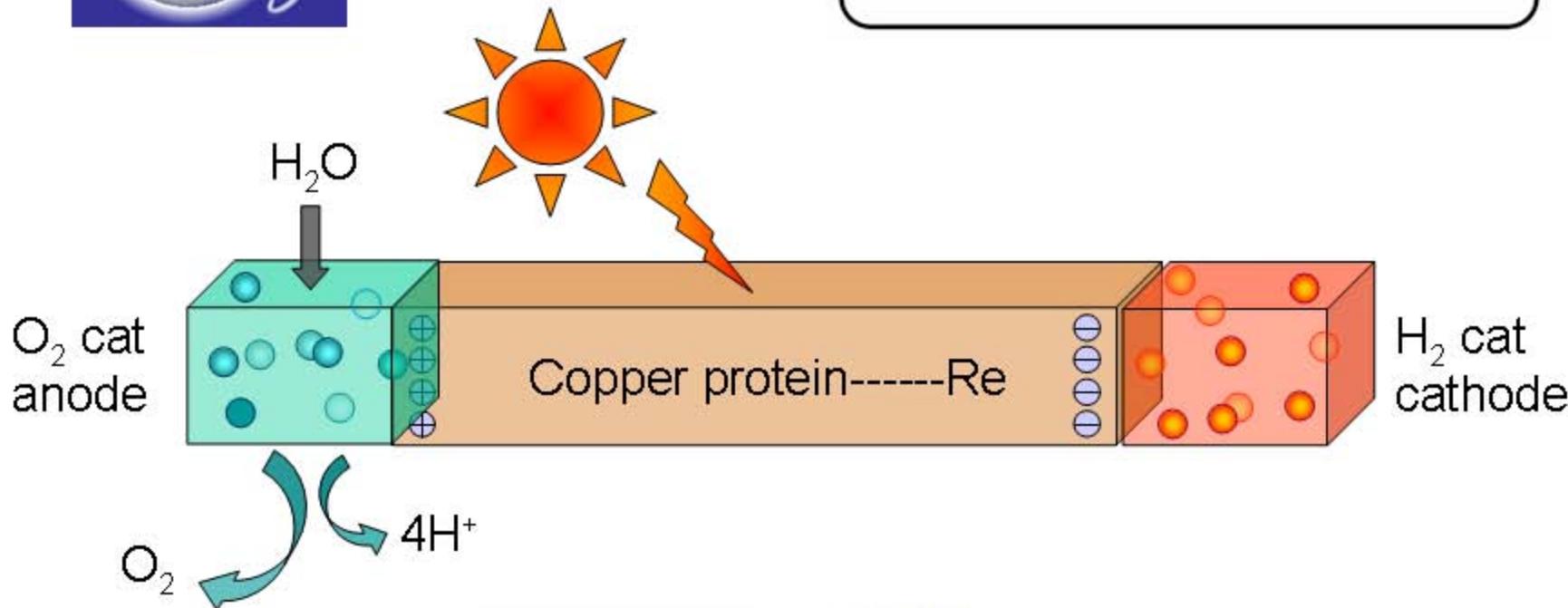
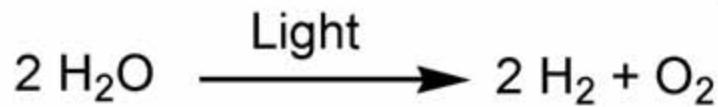
New Jersey- The Garden State

Powering the Planet



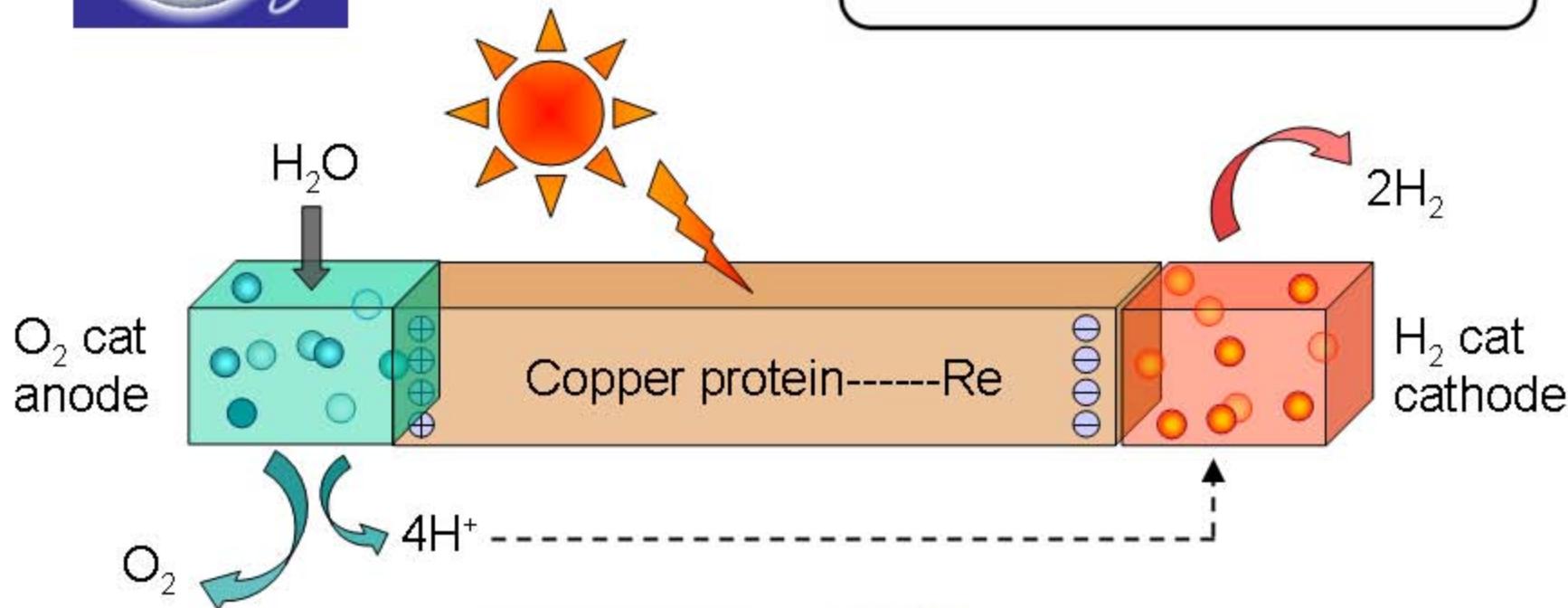
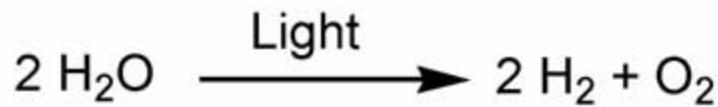
New Jersey - The Garden State

Powering the Planet



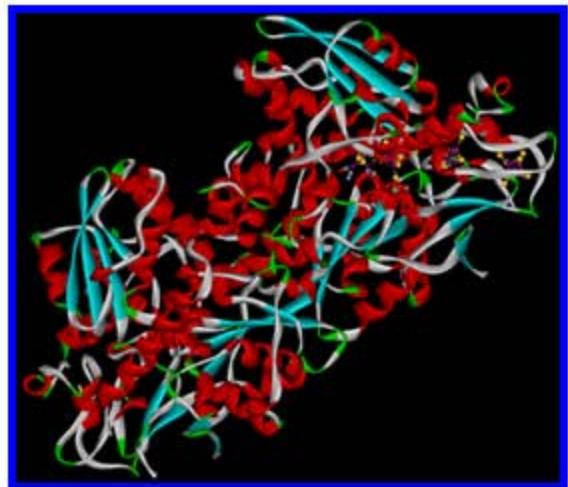
New Jersey - The Garden State

Powering the Planet

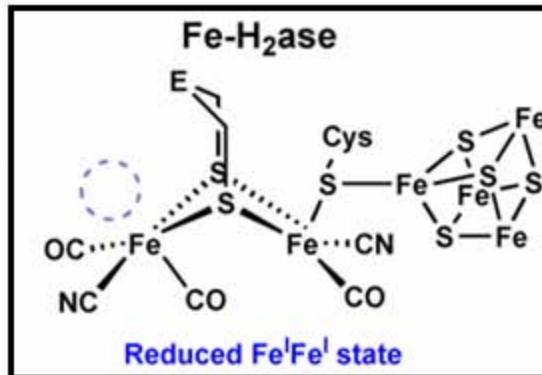
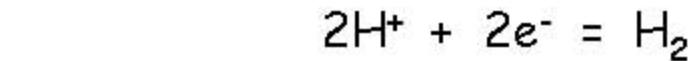


New Jersey - The Garden State

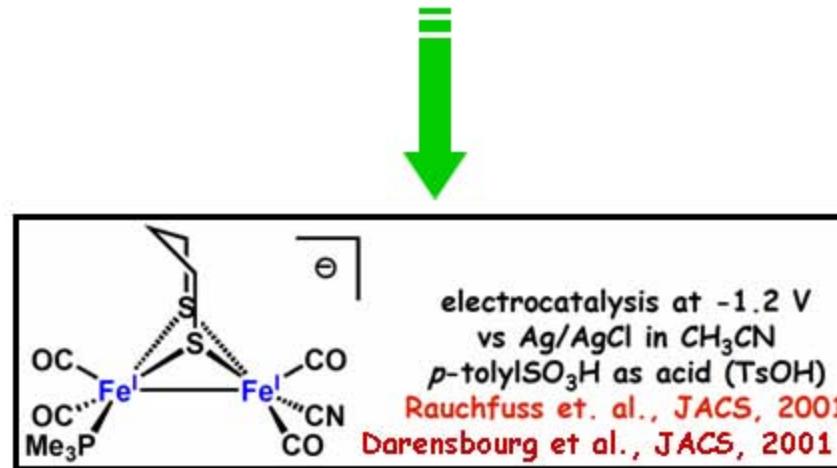
Hydrogenases: Nature makes H₂



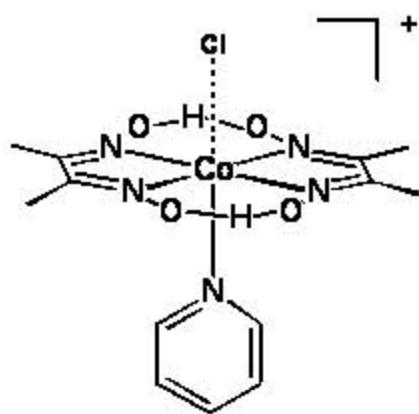
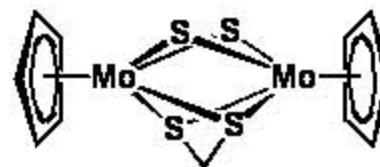
Fe-only H₂ase



$$E^\circ = -420 \text{ mV} (\text{pH} = 7)$$



GRC on Solar Fuels



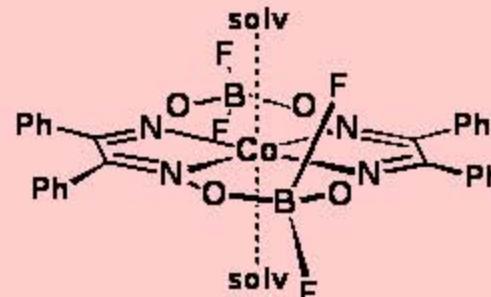
2005

Artero and Fontecave
~ -1.03 V vs SCE in DMF
using HNEt₃⁺ acid (pKa = 9.2)
 $E^\circ(H^+/H_2) = -0.85$ V

2006

DuBois

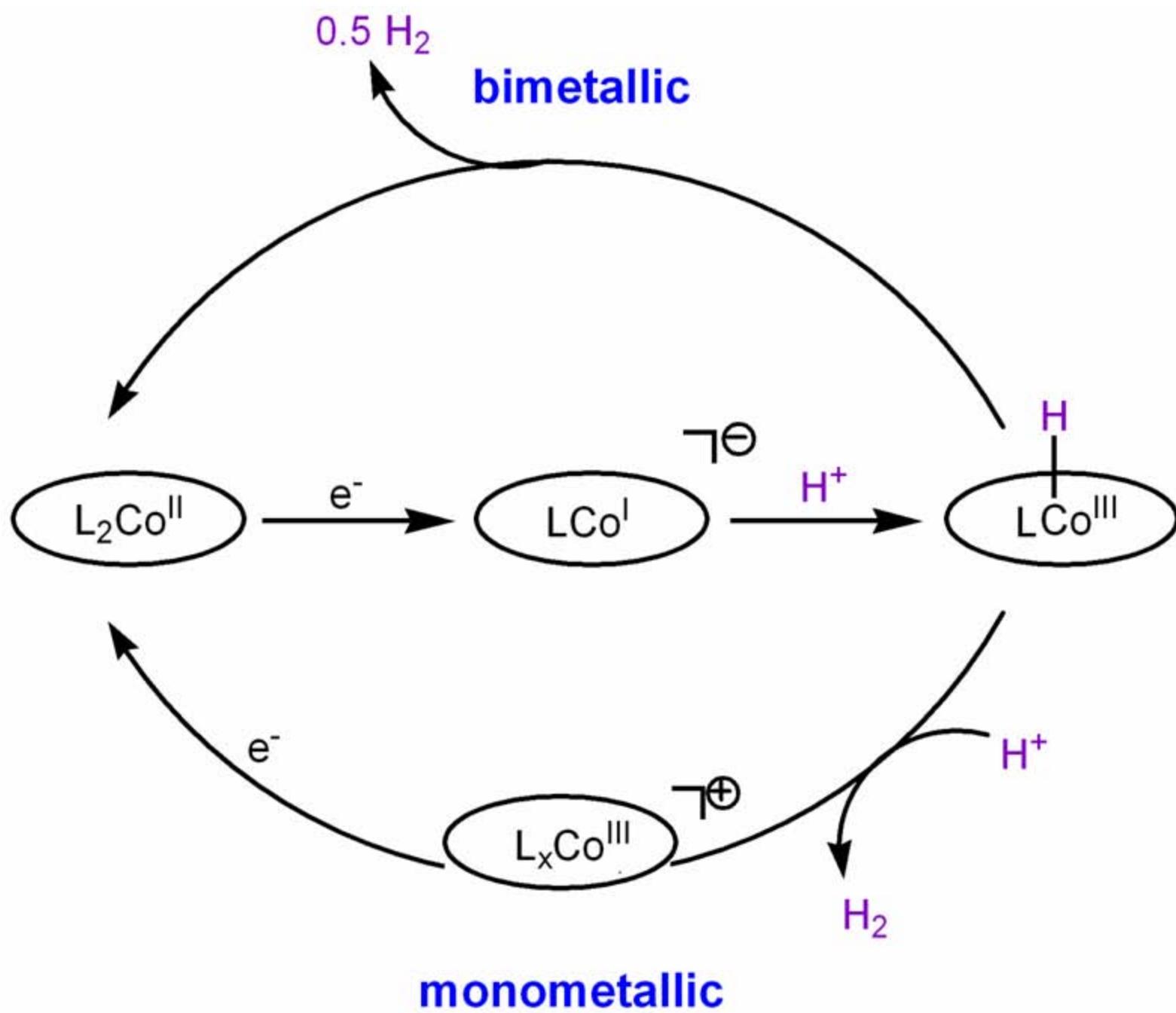
~ -0.25 V vs SCE in CH₃CN
using *p*-CN-anilinium acid (pKa = 7.6)
 $E^\circ(H^+/H_2) = -0.19$ V



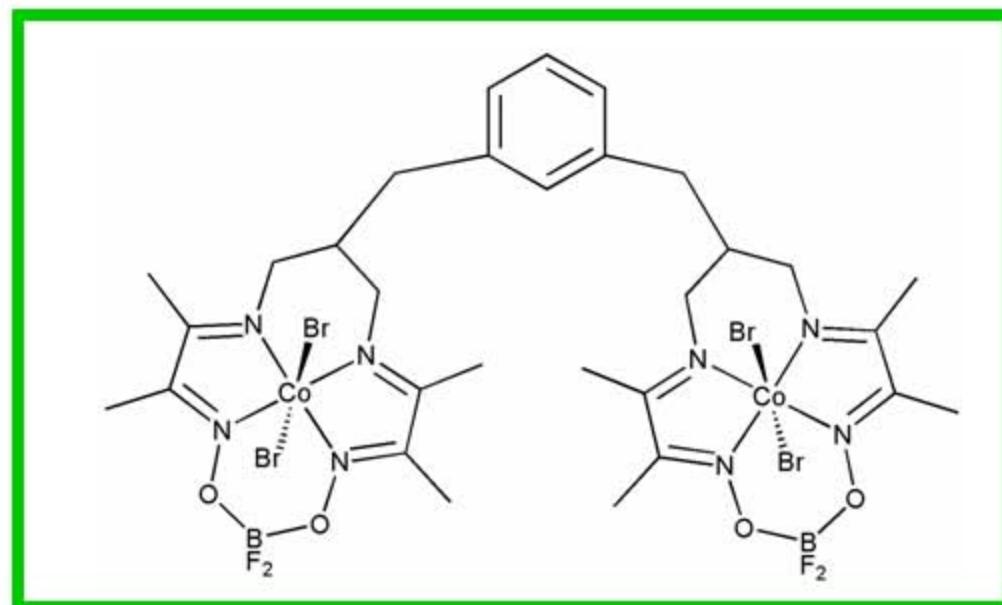
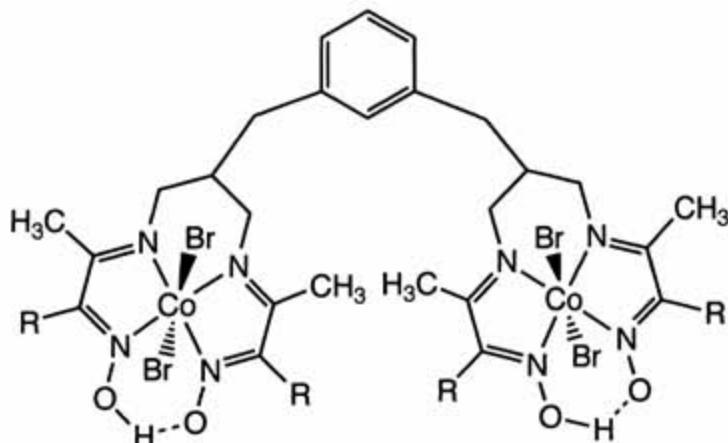
2005

Our efforts at Caltech
~ -0.28 V vs SCE in CH₃CN
using TsOH(H₂O) acid (pKa = 8.7)
 $E^\circ(H^+/H_2) = -0.23$ V





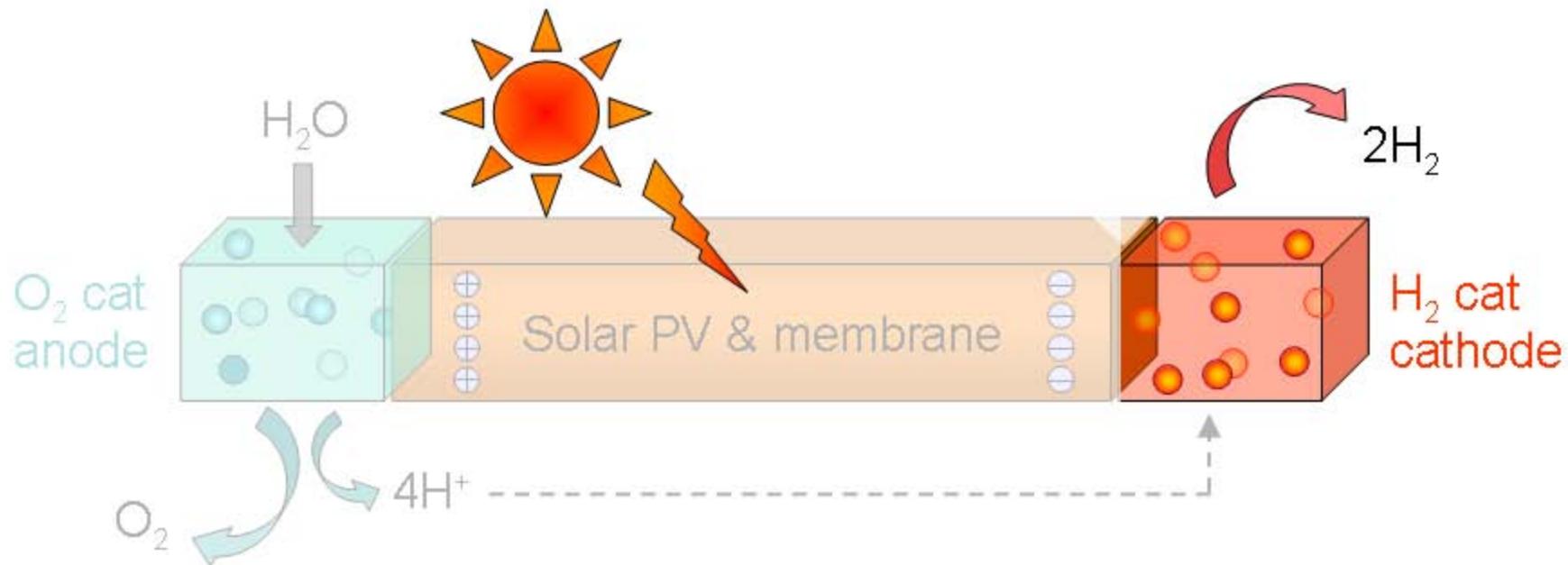
A binuclear catalyst



Carolyn Valdez (SURF)

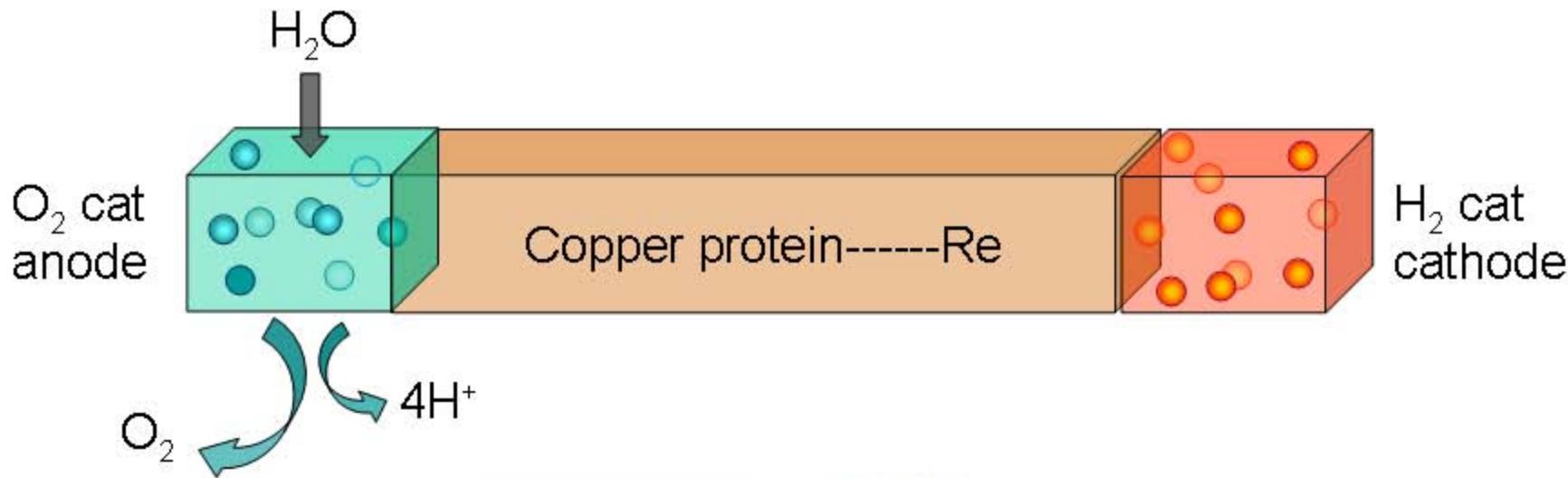
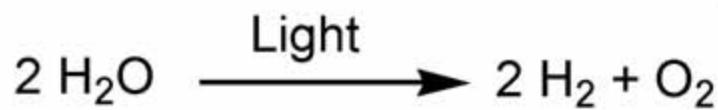
Jillian Dempsey

Hydrogen



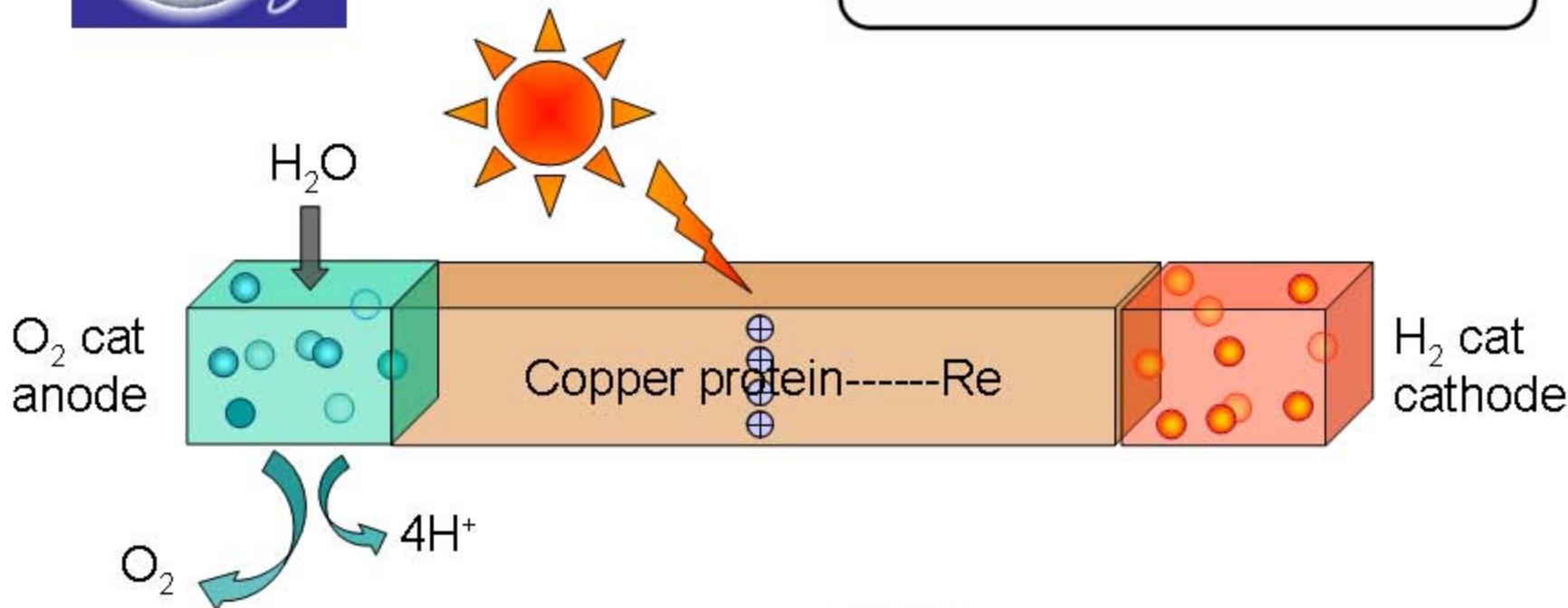
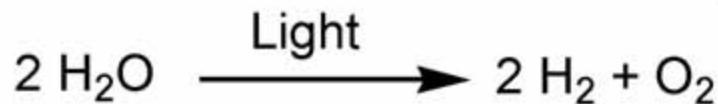
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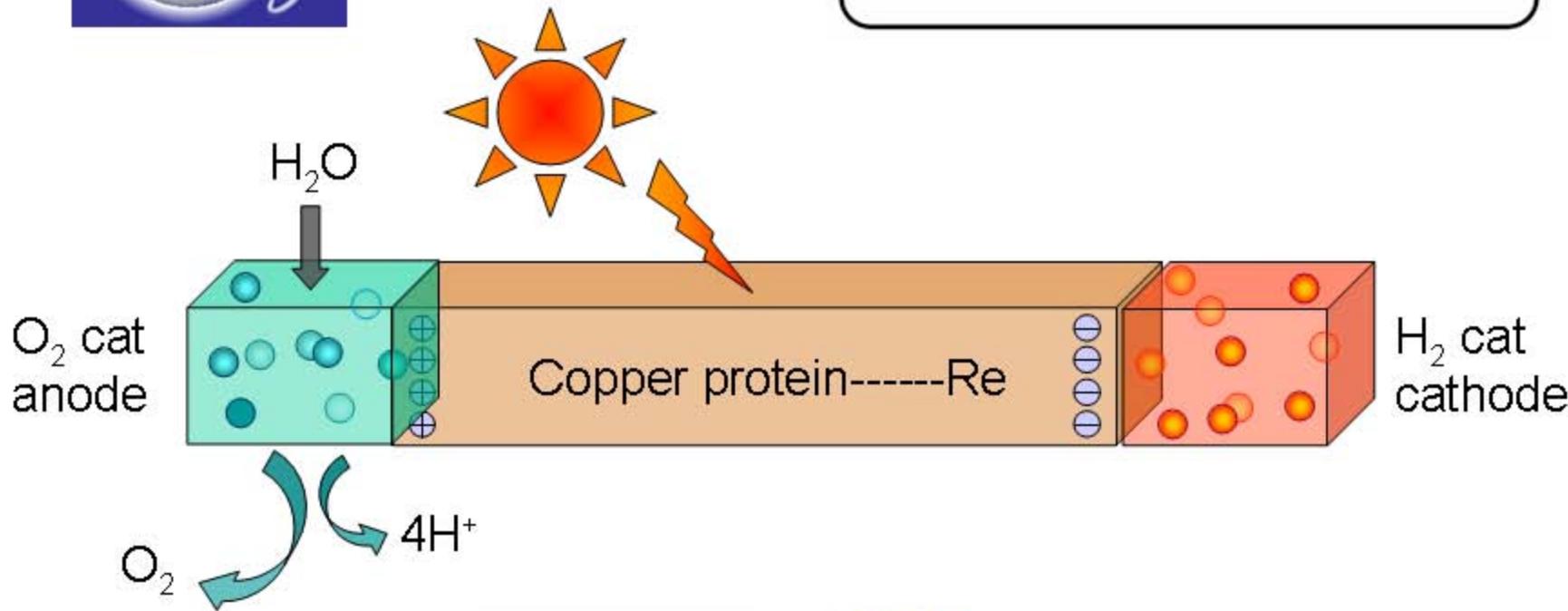
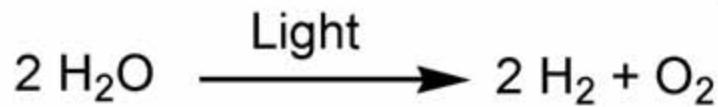
New Jersey- The Garden State

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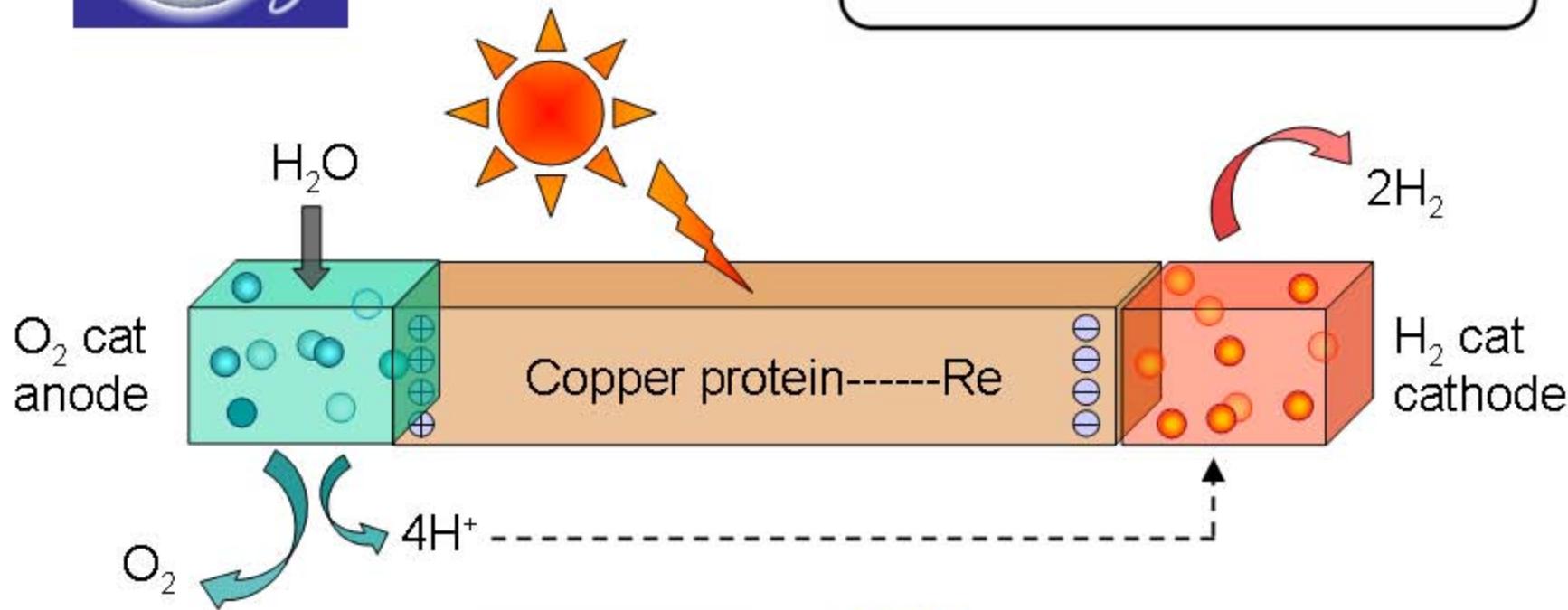
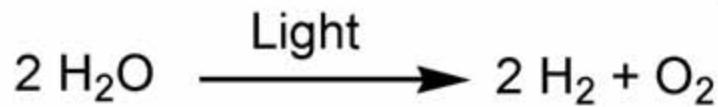
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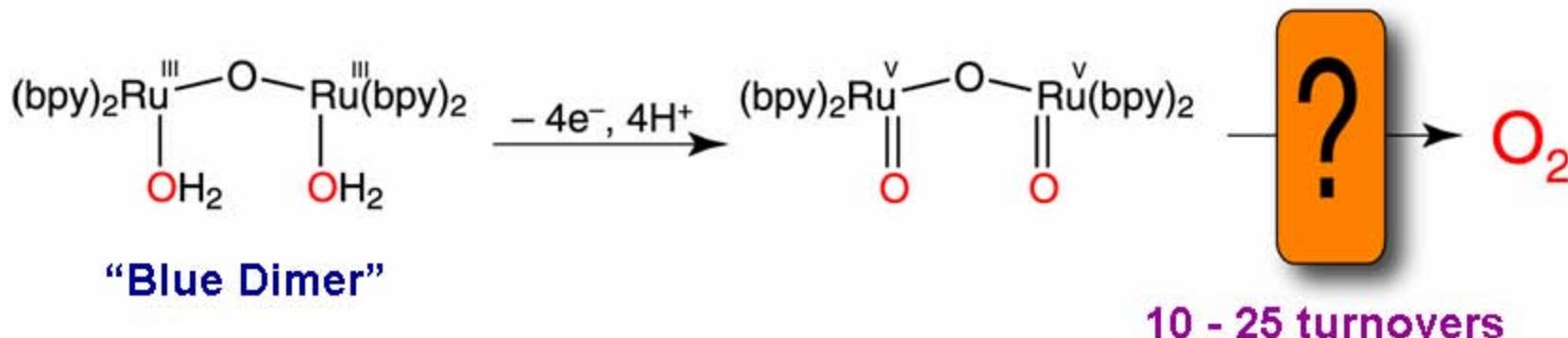
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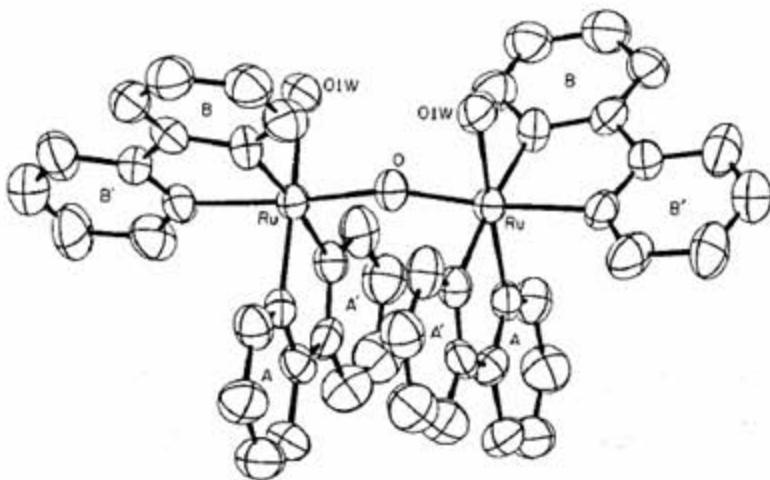


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Water Oxidation Catalysts Are No Good!!



10 - 25 turnovers



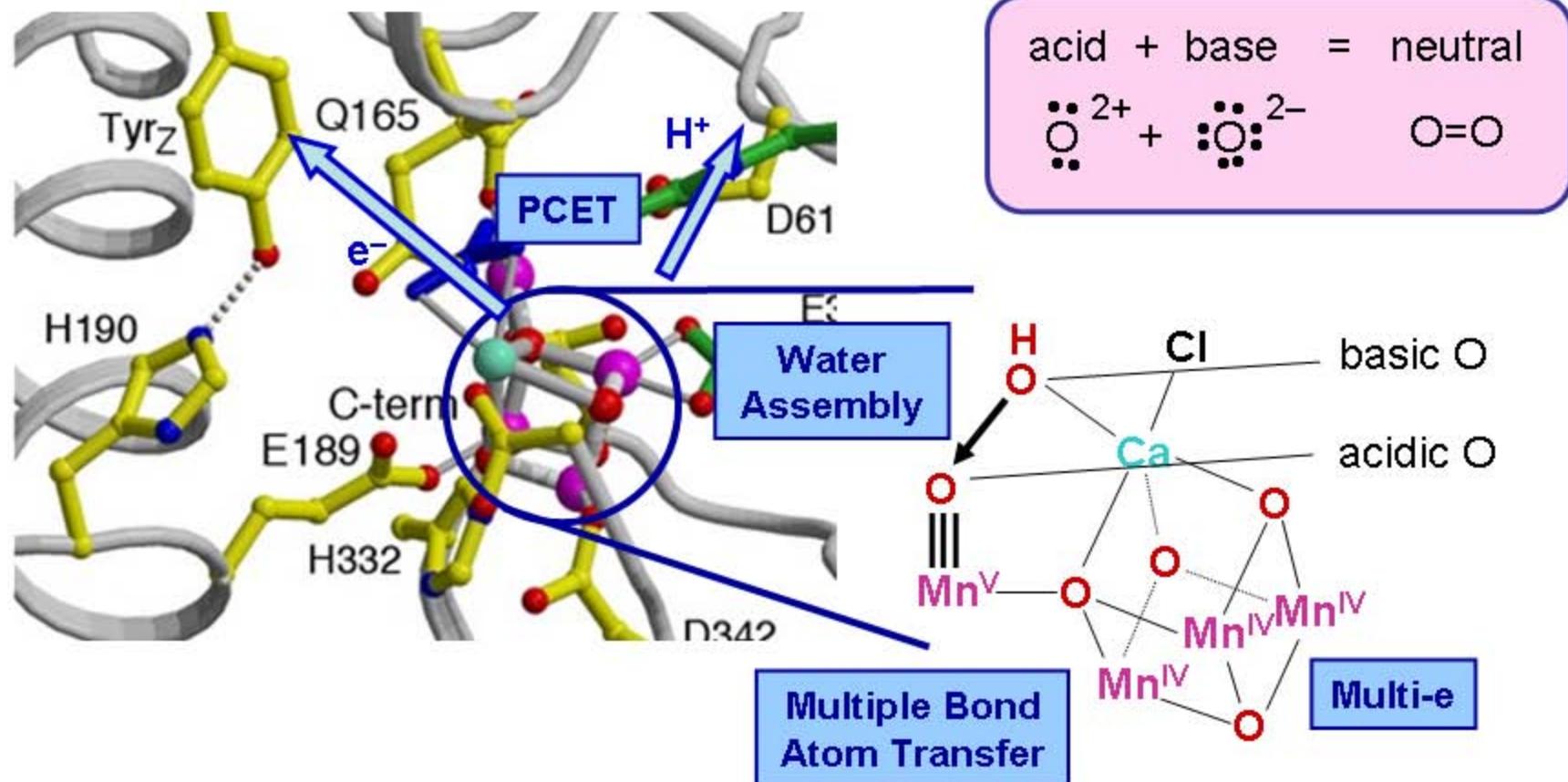
- Only 1 authentic O₂ producing catalyst
- Discovered in 1982 (no progress for a quarter of a century)
- And that catalyst is inefficient (only 25 turnovers)
- Mechanism for O₂ production still unknown

TJ Meyer JACS 1982, 104, 4030



A Clue from Nature

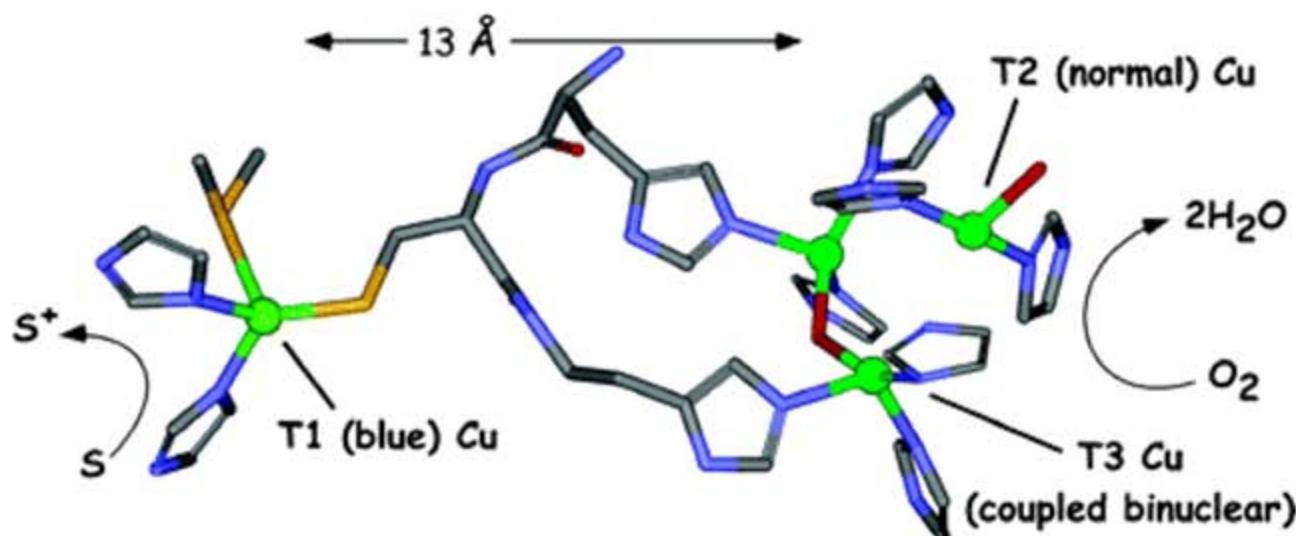
The OEC Active Site of PSII (Imperial College structure)



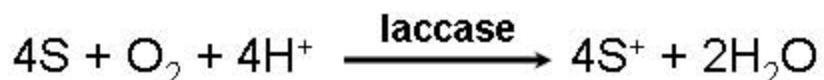
Solar Fuels



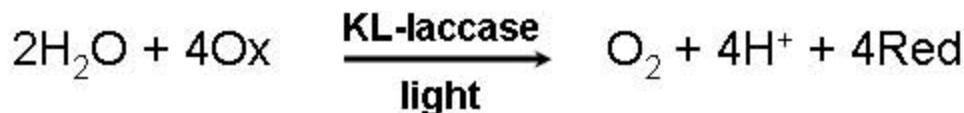
Active Site of Blue Copper Oxidases



Natural Enzymatic Reaction:



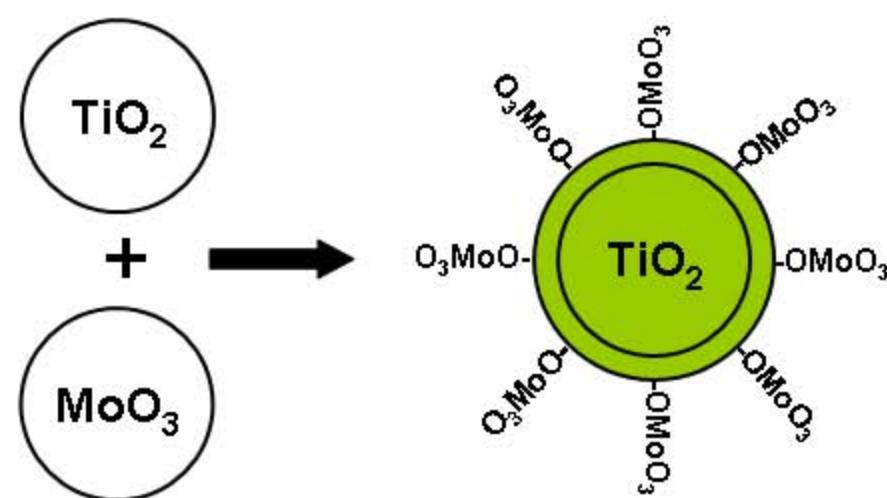
Engineered Enzymatic Reaction:



Solar Fuel

New Directions

Robust Materials
Water Splitting



Mixed-Oxide Nanoparticles



Powering the Planet

NSF Chemical Bonding Center

CALTECH TEAM



Gray (PI)



Brunschwig



Winkler



Lewis

MIT TEAM



Cummins



Nocera



Peters



Don Walker

Jillian Dempsey

Carolyn Valdez

Crystal Shih

Keiko Yokoyama

Kyle Lancaster

Josh Palmer

Bryan Stubbert



NSF
CCSER

Harry Atwater

Sossina Haile

Nate Lewis

Jay Winkler

Bruce Brunschwig

Corey Wilson

Craig Wiggenhorn

Kristine Kilså



Hydrogen Power!!



Q'orianka Kilcher is the 2nd individual leaser of a Honda FCX
Honda hopes to have the FCX in “low rate” production by 2008
Currently there are 16 H₂ fueling stations in CA under the CA Fuel Cell Partnership

