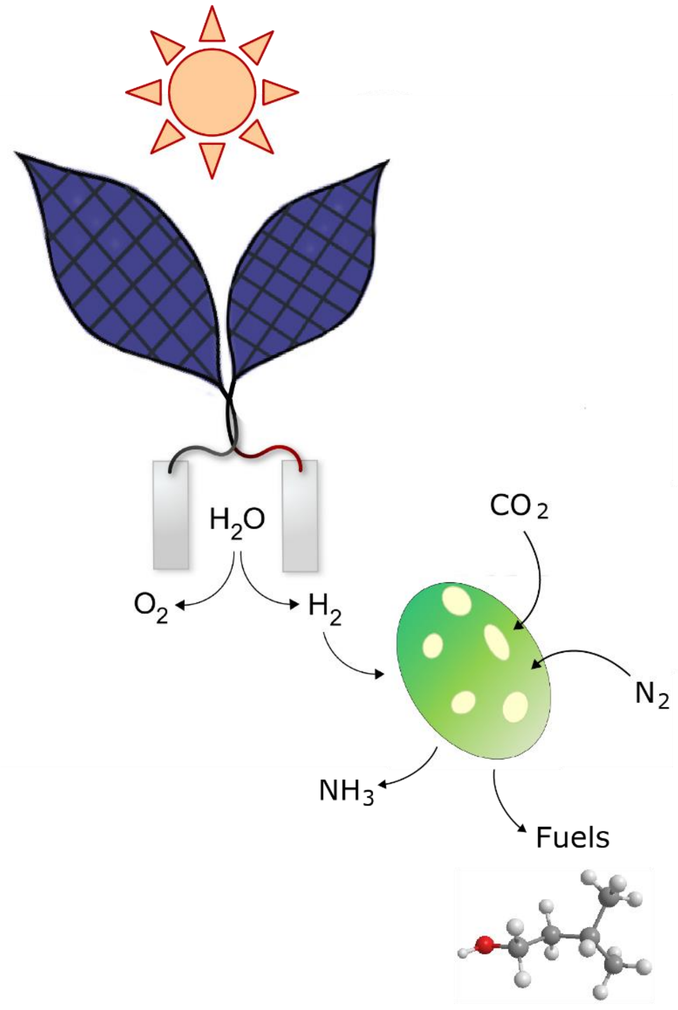
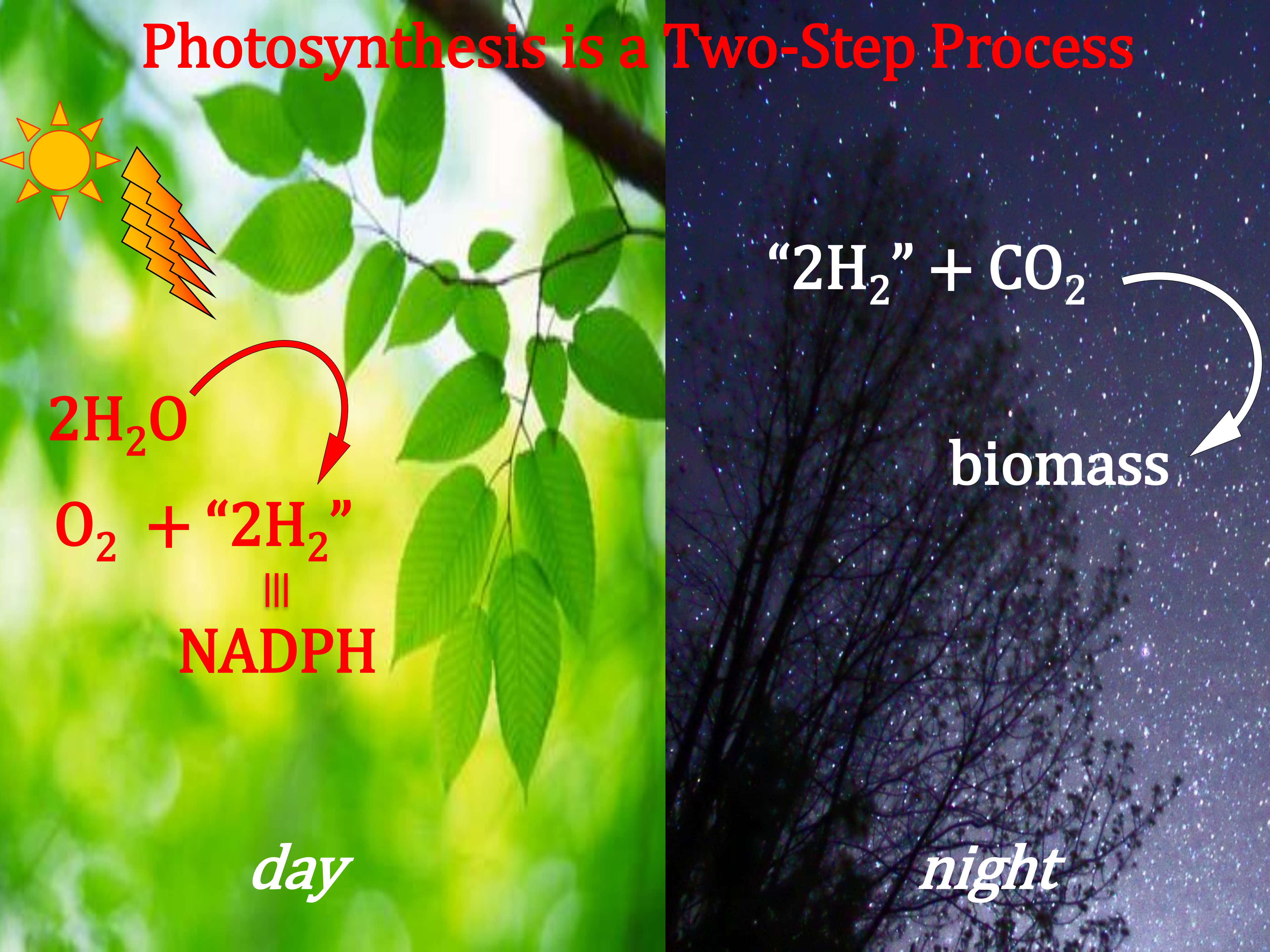
Department of Chemistry and Chemical Biology
Harvard University

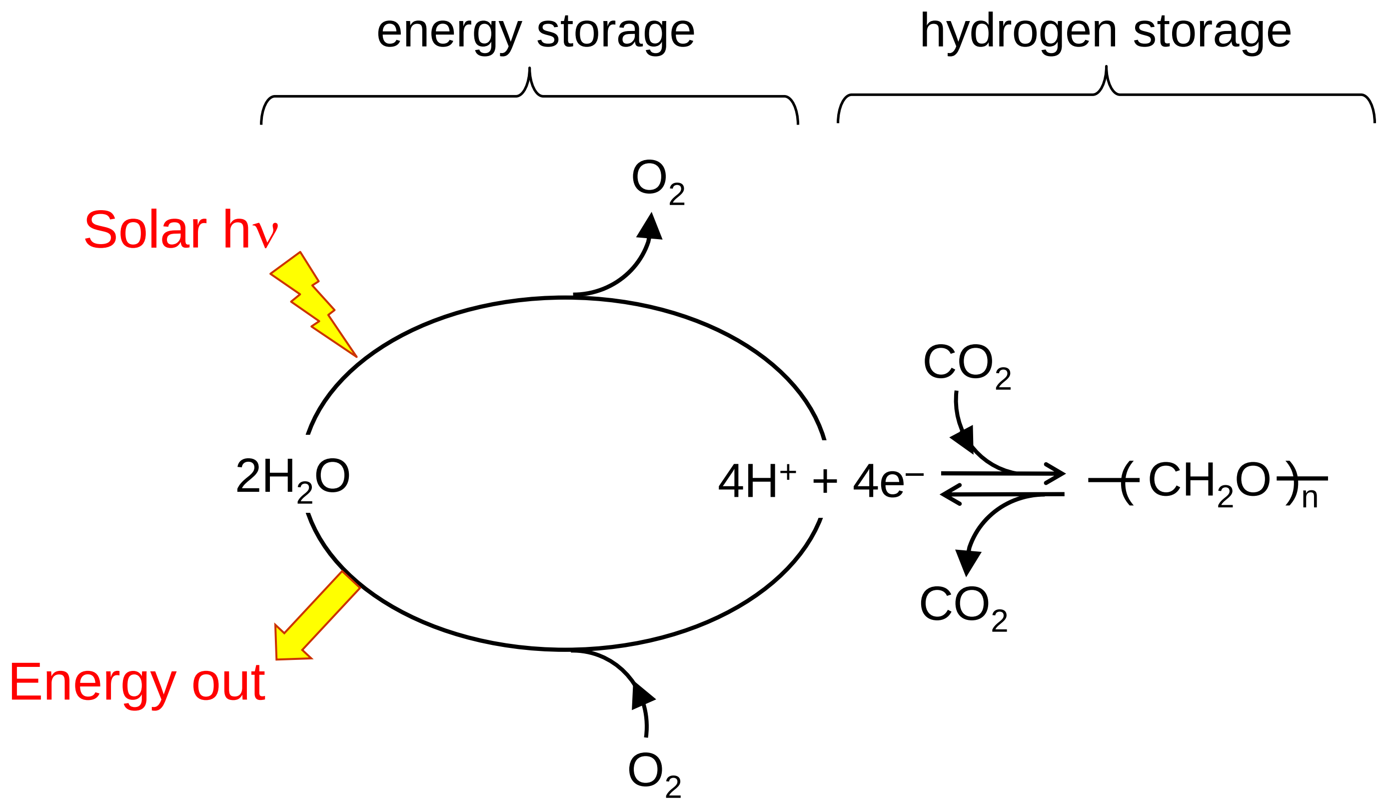
Artificial Leaf and Bionic Leaf

Fuel and Food Sunlight, Air and (Any) Water




Photosynthesis is a Two-Step Process
$2H_2O$
O_2 + "$2H_2$"
|||
NADPH
"$2H_2$" + CO_2
biomass
day
night

Two Step Process to Achieve Complete Artificial Photosynthesis



Thermodynamics of Fuel Formation

$$G^{o} = -nFE^{o}$$

Water splitting to furnish H^+/e^- (H_2) is thermodynamically uphill:

$2H_2O \rightarrow O_2 + 2H_2$ ($4H^+ + 4e^-$) $E^{o} = -1.23$ V

CO_2 reduction with hydrogen to fuels is thermoneutral:

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ $E^{o} = 0.17$ V

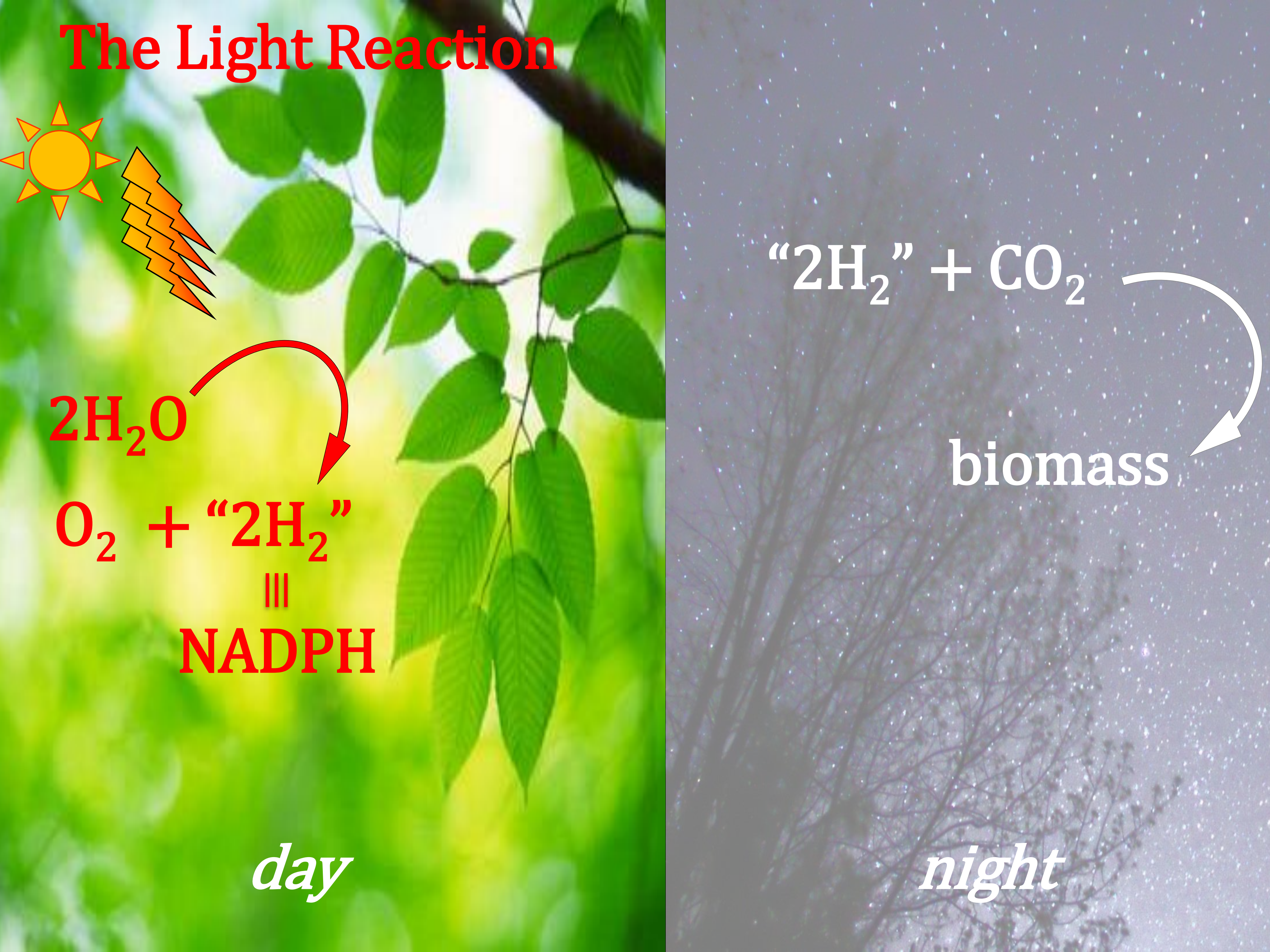
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$ $E^{o} = 0.03$ V

$3CO_2 + 18H^+ + 18e^- \rightarrow i\text{-}C_3H_7OH + 5H_2O$ $E^{o} = 0.09$ V

$4CO_2 + 24H^+ + 24e^- \rightarrow i\text{-}C_4H_9OH + 7H_2O$ $E^{o} = 0.11$ V

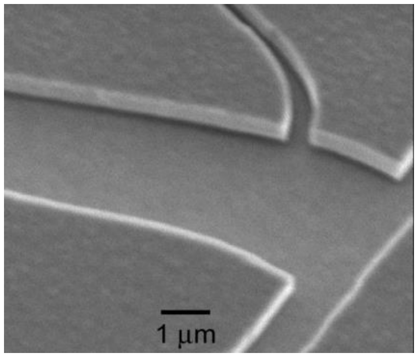
$5CO_2 + 30H^+ + 30e^- \rightarrow i\text{-}C_5H_{11}OH + 9H_2O$ $E^{o} = 0.08$ V

Chaplin and Wragg, *J. Appl. Electrochem.* **2003**, *33*, 1107

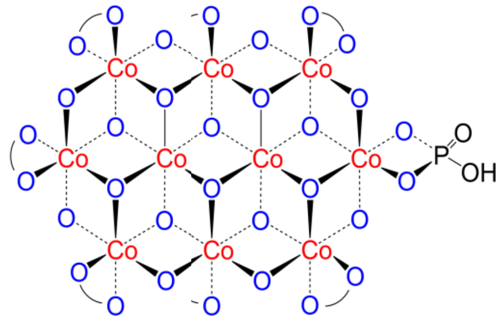

The Light Reaction
$2H_2O$
O_2 + "$2H_2$"
|||
NADPH
day
"$2H_2$" + CO_2
biomass
night

Self Healing Water Splitting

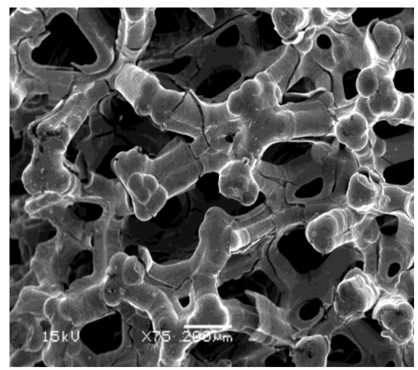
$2H_2O$ → $O_2 + 4e^- + 4H^+$



Co phosphate oxide



$2H_2$ ←



3-metal alloy, NiMoZn
or Co-P(6%) alloy

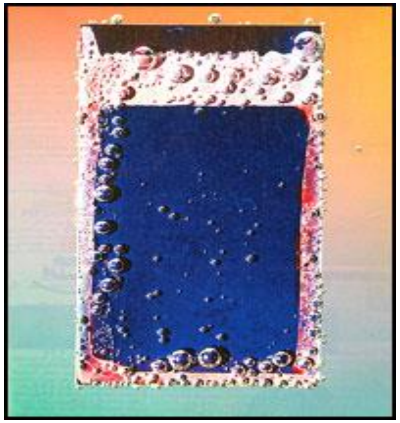
❖ Two catalysts: one to split water to oxygen, the other to take the leftover protons and electrons to make hydrogen

But how can sunlight drive these catalysts?

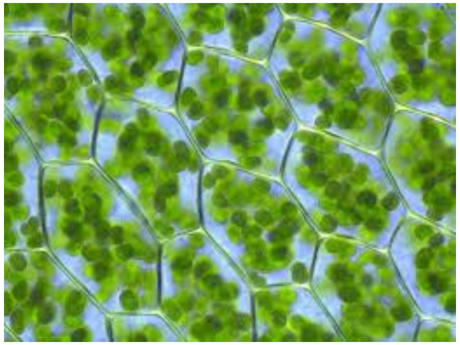
Self-Healing Enables …

operation under benign conditions and with any water source

(Boston Harbor, Charles River, waste water, puddle from the ground)

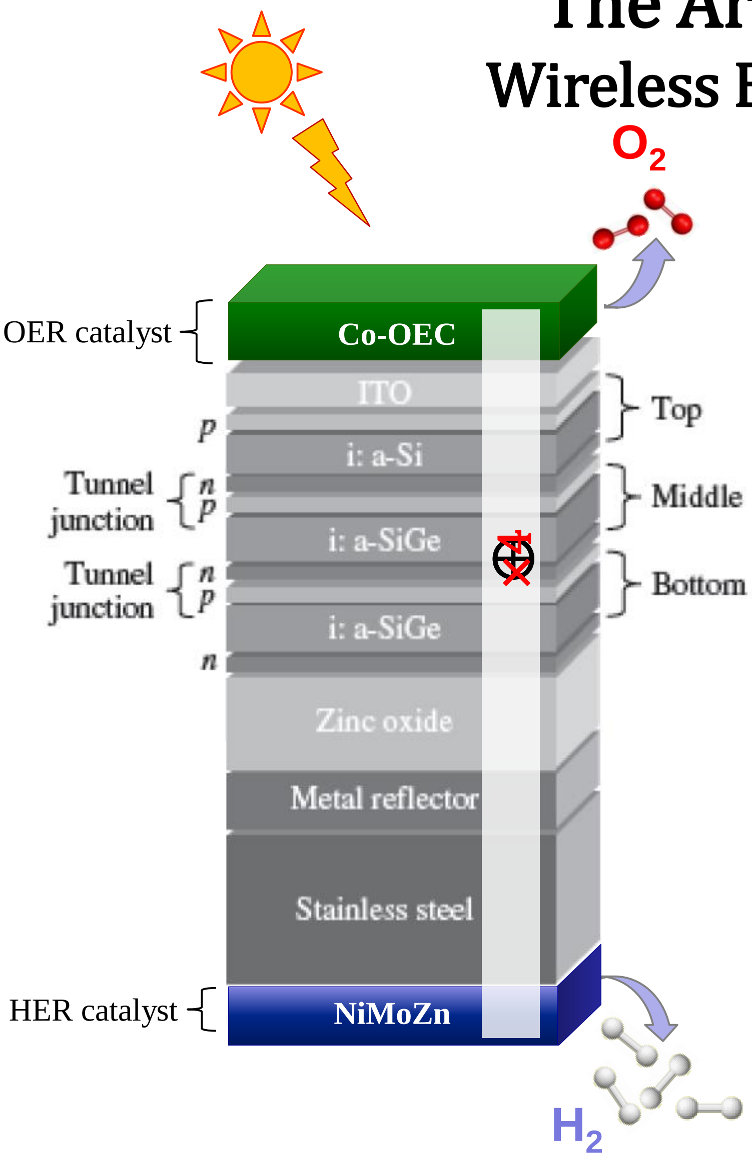


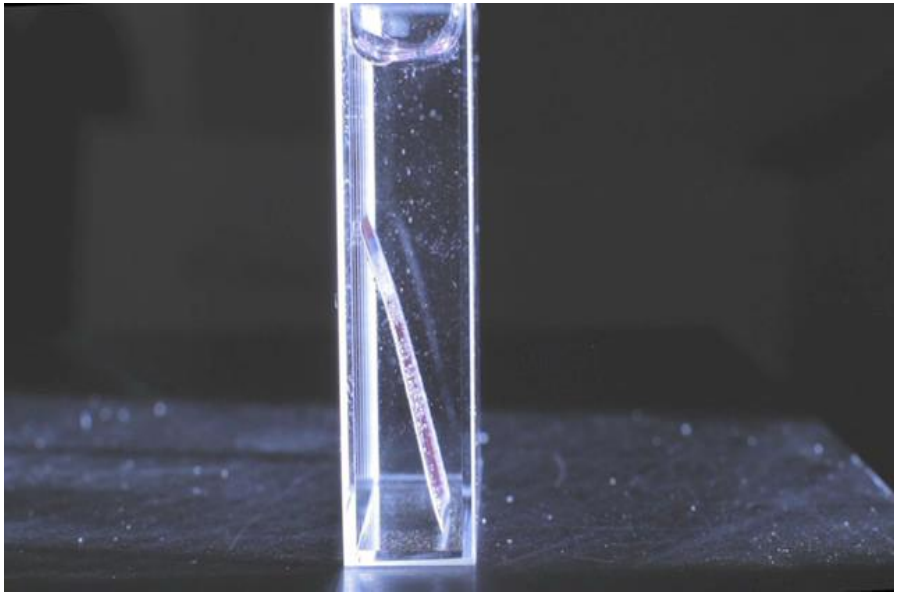
facile construction of integrated devices



interface with bioorganisms

The Artificial Leaf
Wireless Buried Junction





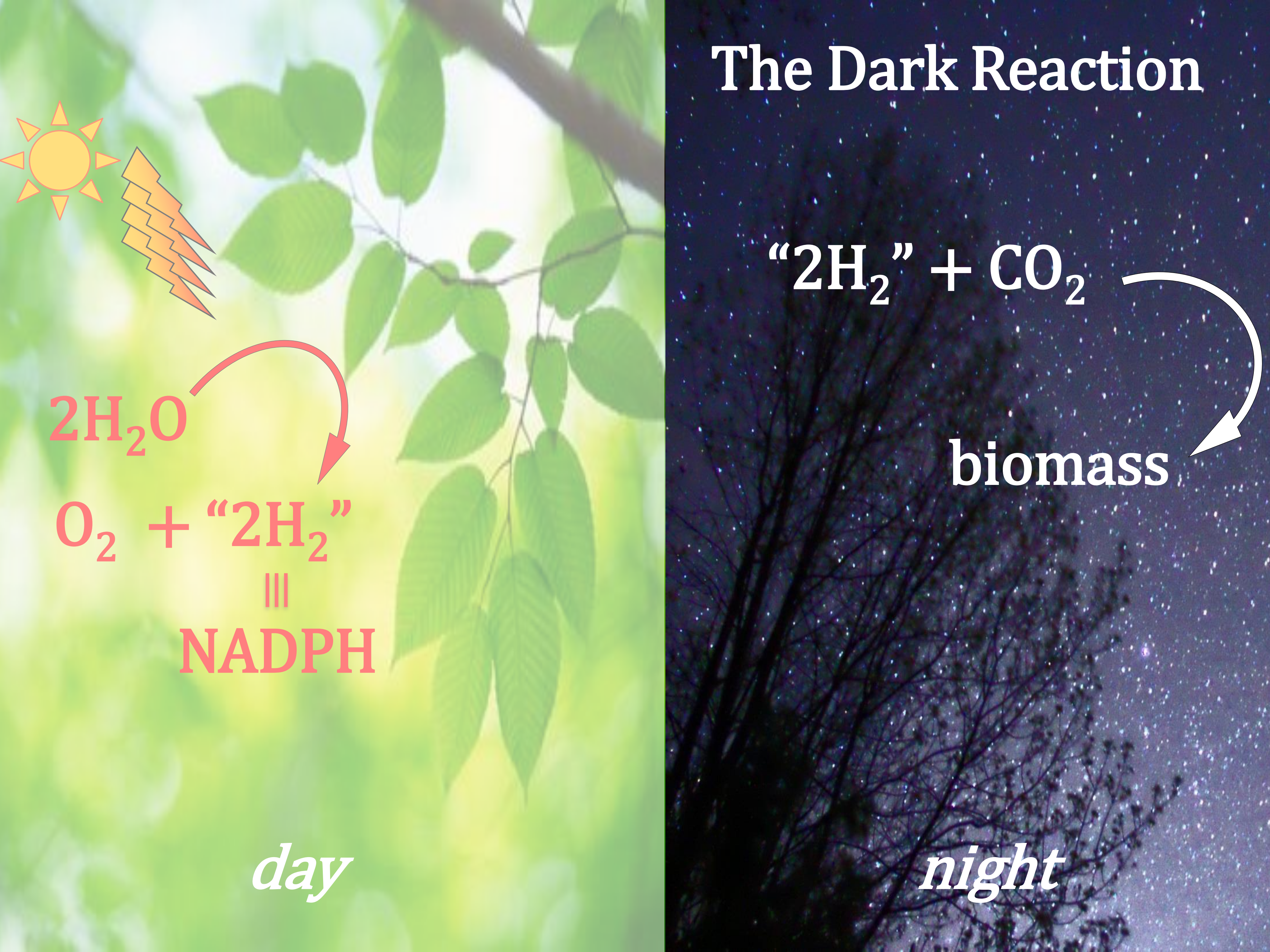
- Only coatings – no wires
- Works at solar flux
- **STH of 12.8%**

Steve Reece
Lockheed Martin

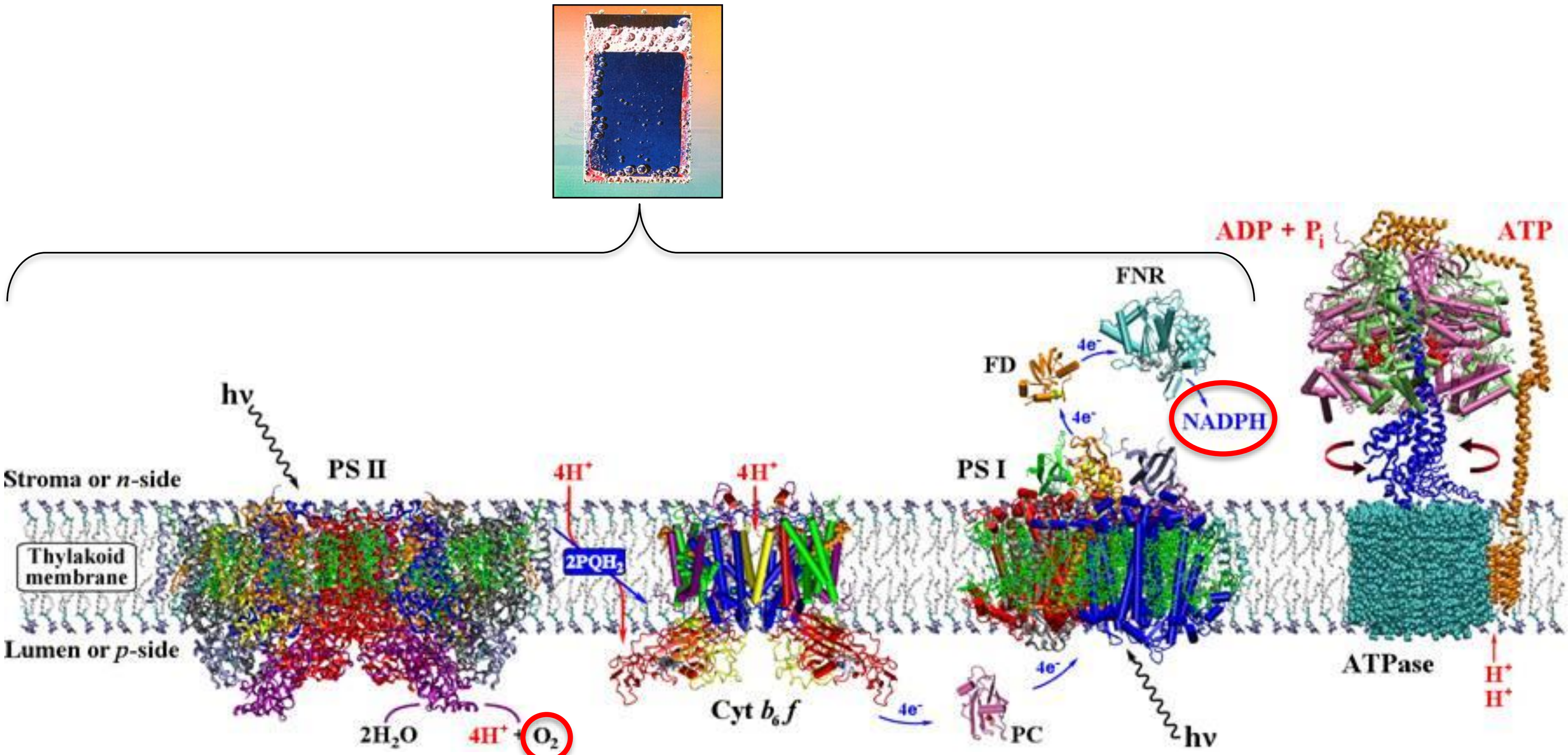
Tuncay Özel
Apple

Casandra Cox
BASF

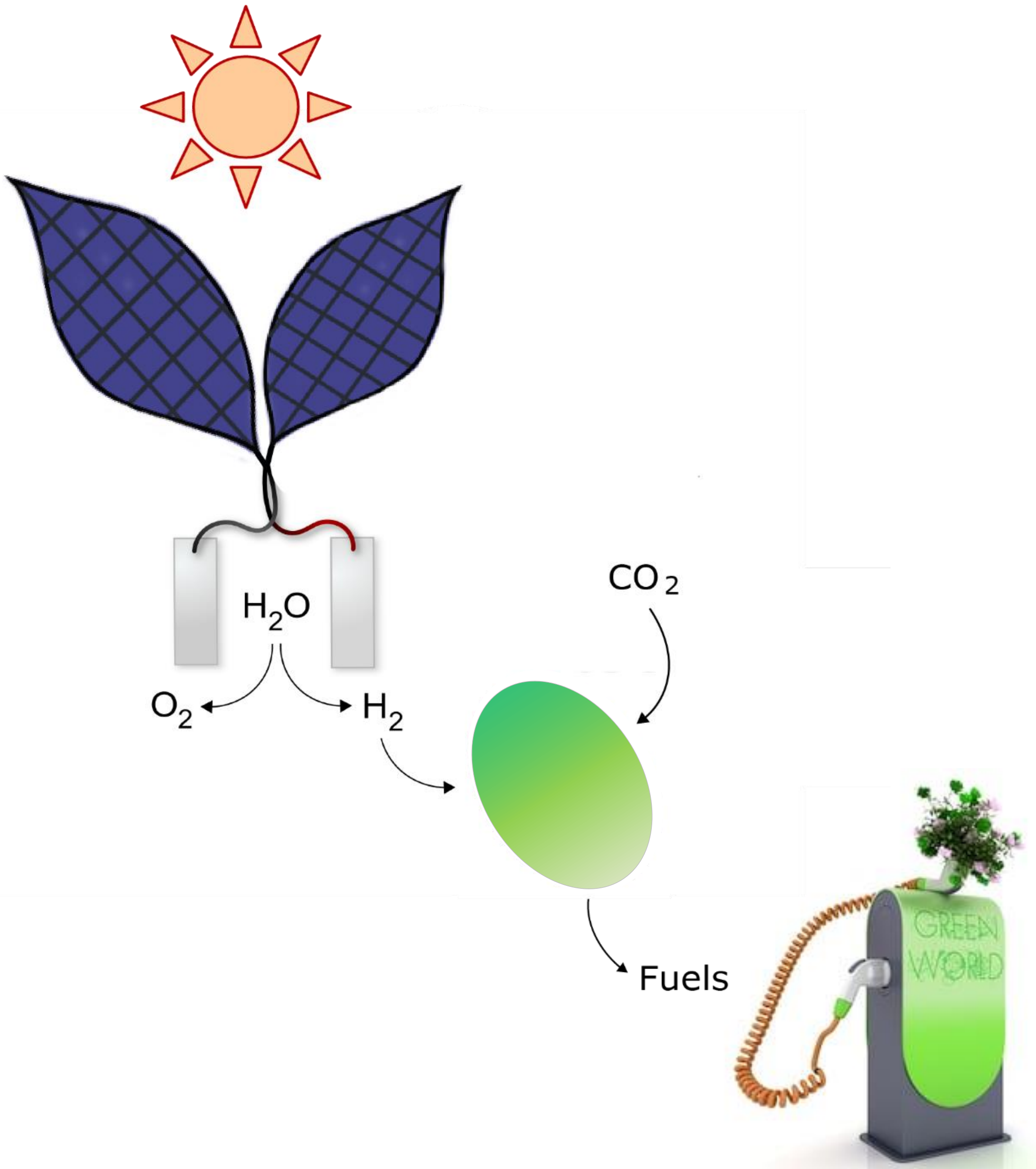
Joep Pijpers
SENER


The Dark Reaction
$2H_2O$
O_2 + "$2H_2$"
|||
NADPH
"$2H_2$" + CO_2
biomass
day
night

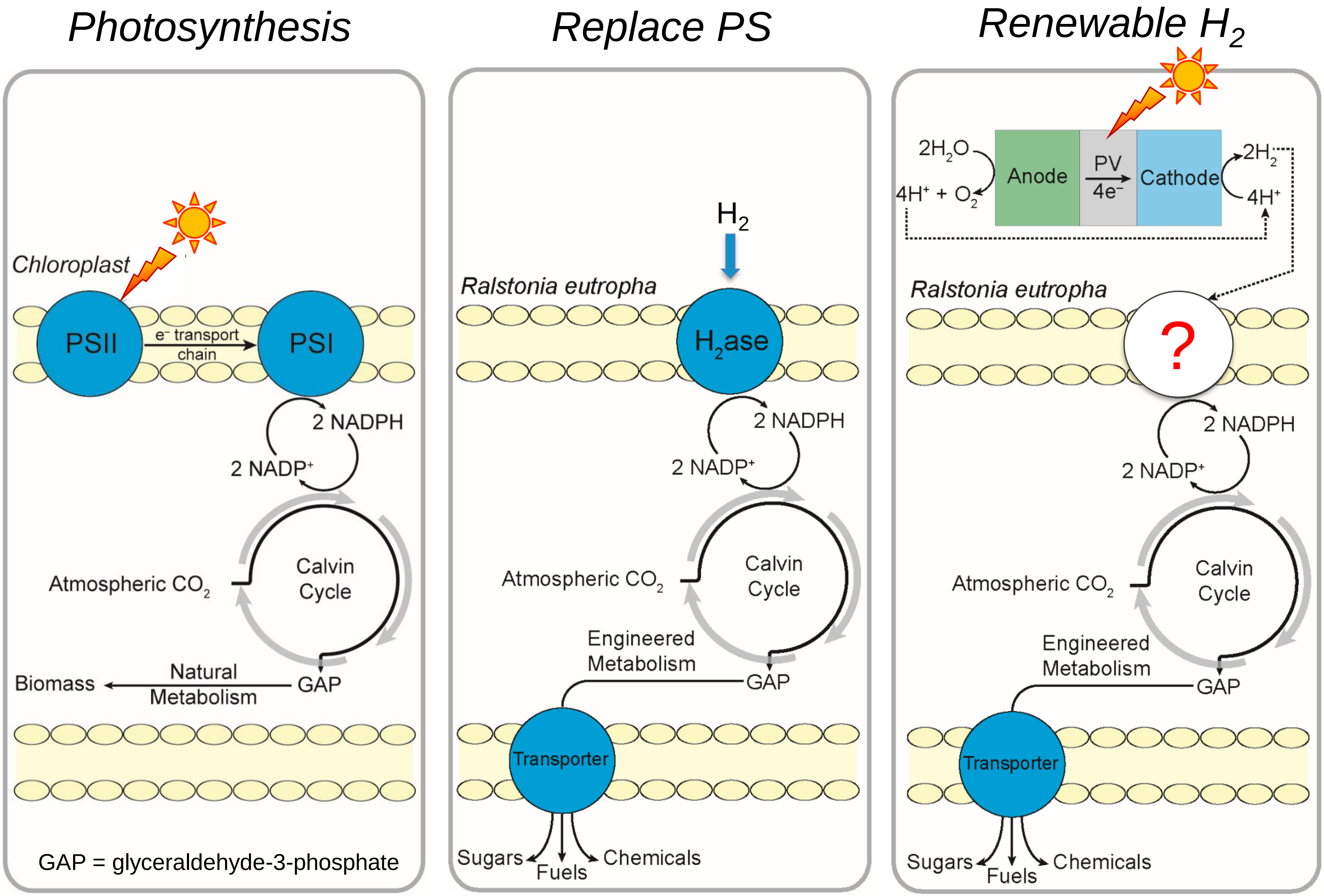
Photosynthetic Membrane
PS I and PSII Replaced with the Artificial Leaf



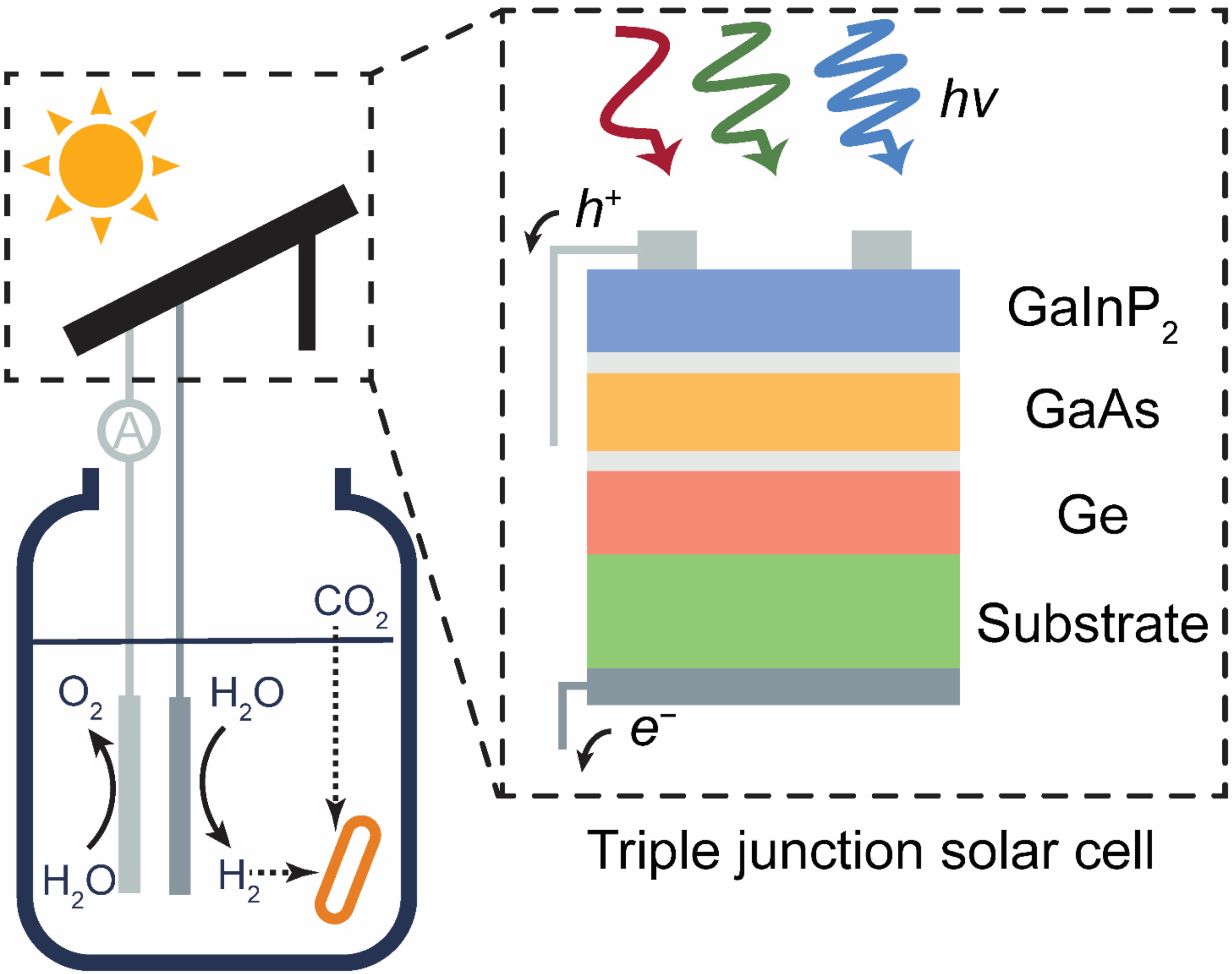
Bionic Leaf 1
(Water Splitting + Carbon Fixing Organisms)



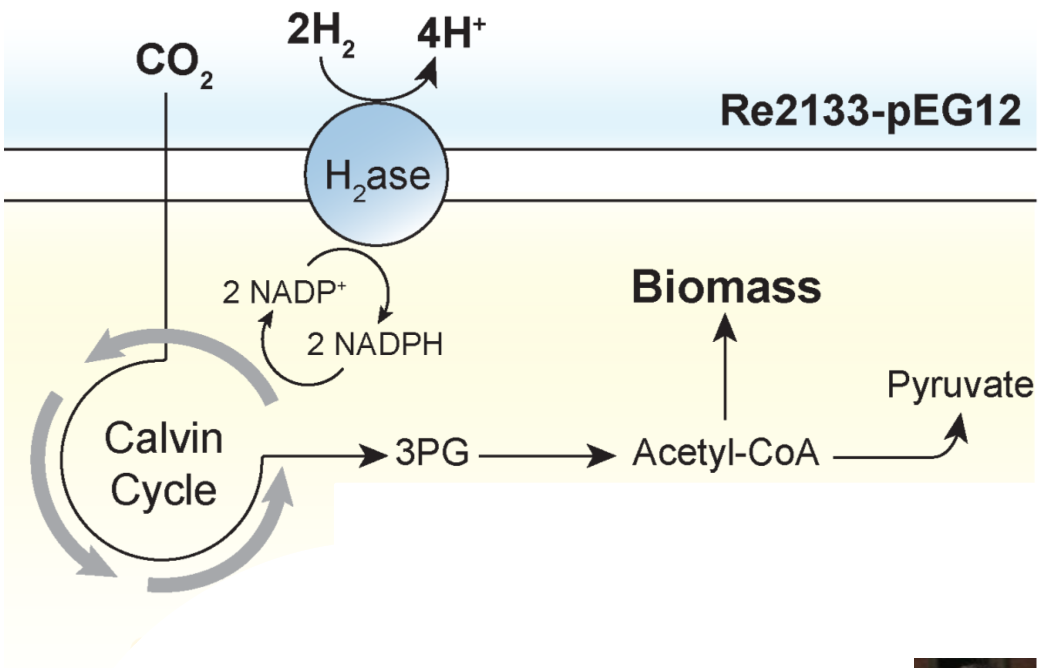
Natural Photosynthesis → All Artificial Photosynthesis



The Bionic Leaf



Re-engineered *R. eutropha* for Isopropanol Production

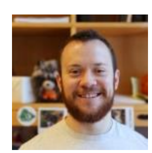


wt R. eutropha
converts acetyl-CoA to biomass and polyhydroxy-butyrate (PHB)

Chris Gagliardi
LEK Consulting

Joe Torella
Boston Consulting

Chong Liu
Asst Prof
UCLA



Brendan Colón
Amazon

Energy Efficiency Calculation

$$\eta_{elec} = \frac{\Delta_r G^o \times N}{C \times E_{appl}}$$

← Gibbs free energy of CDR x moles of product

← electric energy input for H_2 production
charge passed x voltage for water splitting

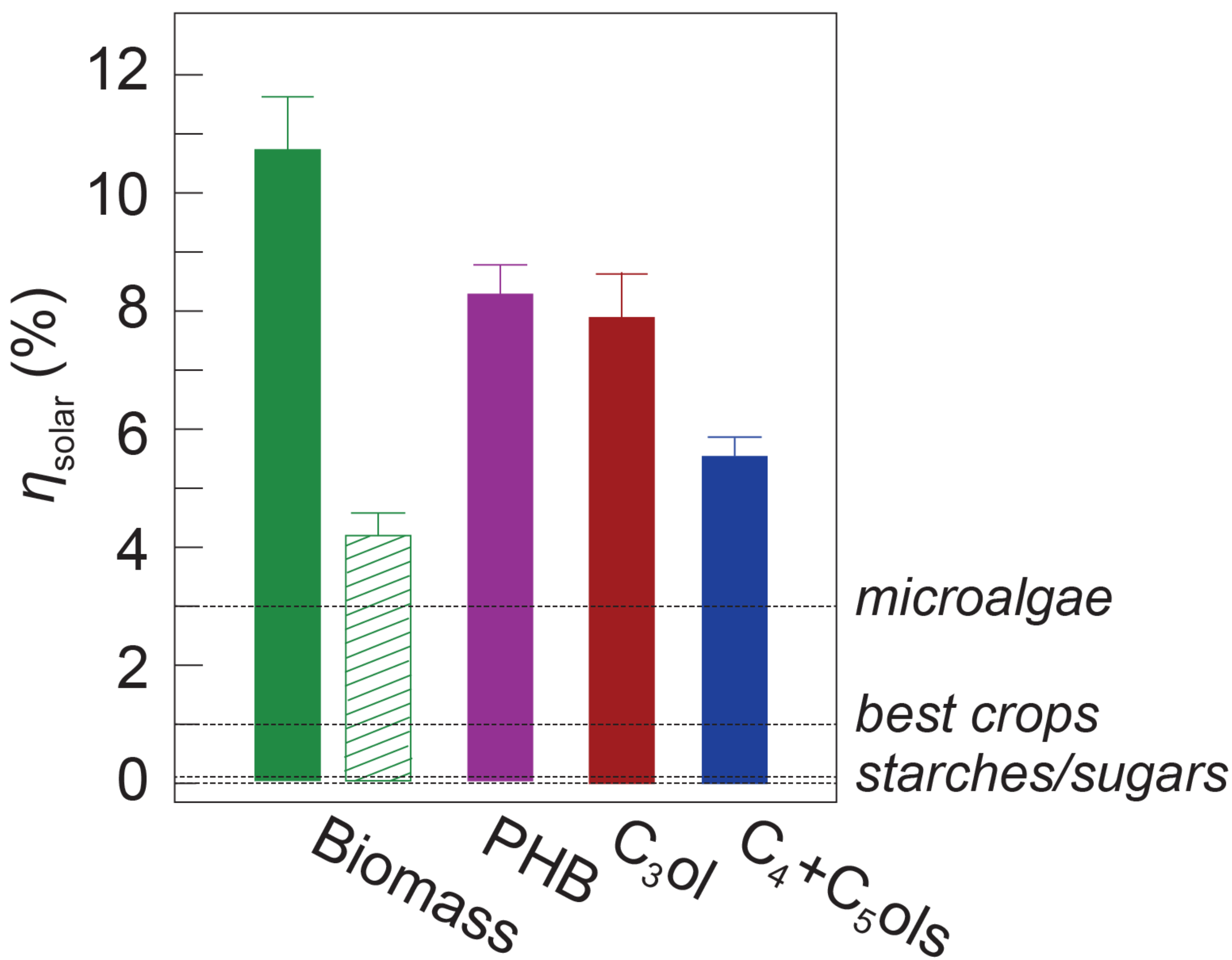
For isobutanol:

$$4CO_2(g) + 5H_2O(\ell) \longrightarrow C_4H_{10}O\,(\ell) + 6O_2(g)$$

$\Delta_r G^o$ (kj mol^{-1})	N(mol)	$\Delta_r G$ (kj)	C(Coul.)	E_{appl} (V)	C x E (kJ)	η_{elec}
+1951	8.98×10^6	1.56	2510	2.0	5.02	31%

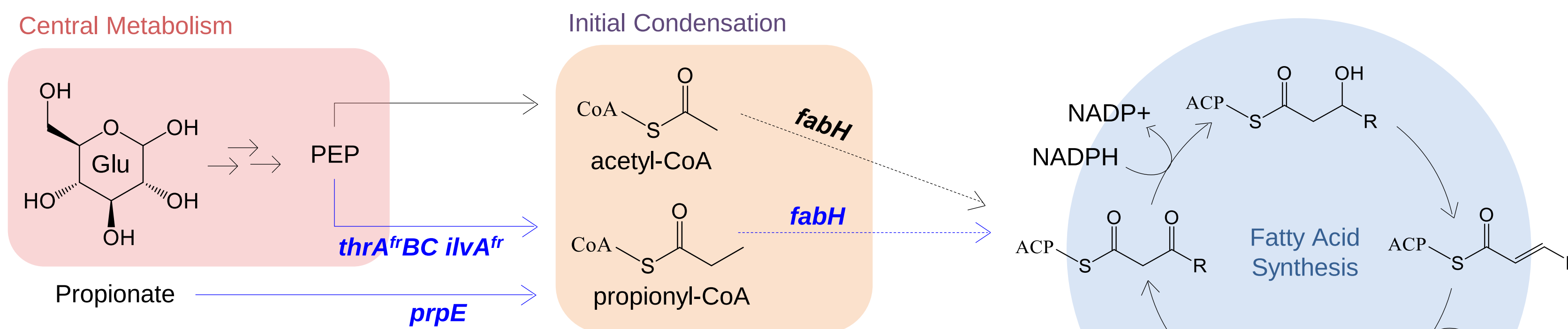
➡ for an 20% PV, 6.0% SFE

Bionic Leaf is Ten Times Better than Natural Photosynthesis

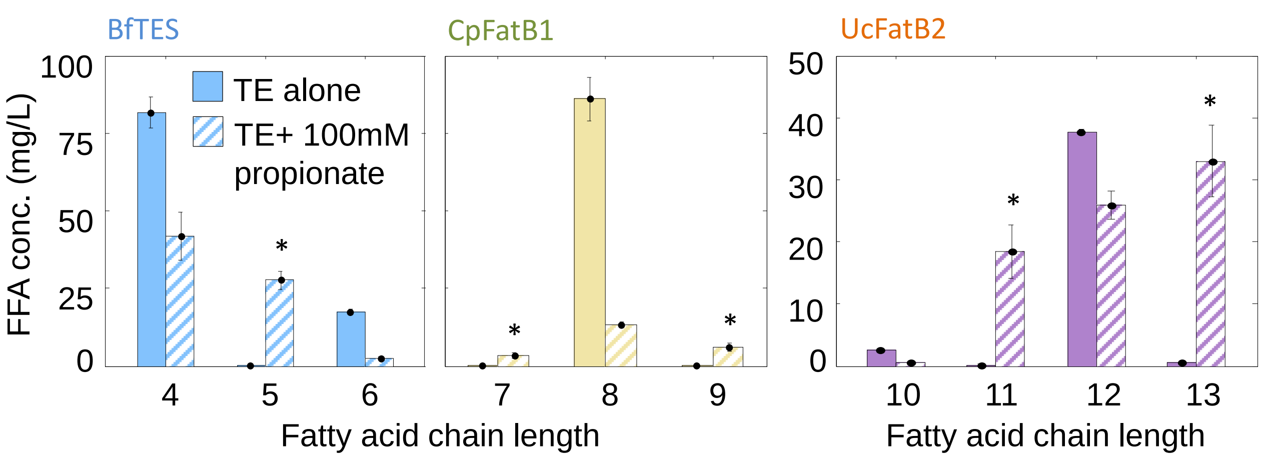


C10+ Fuels

4 C initially, then add 2 C at a time



medium chain FA selectivity by altering thioesterase



Nitrogen: Another Biogenic Element in Air

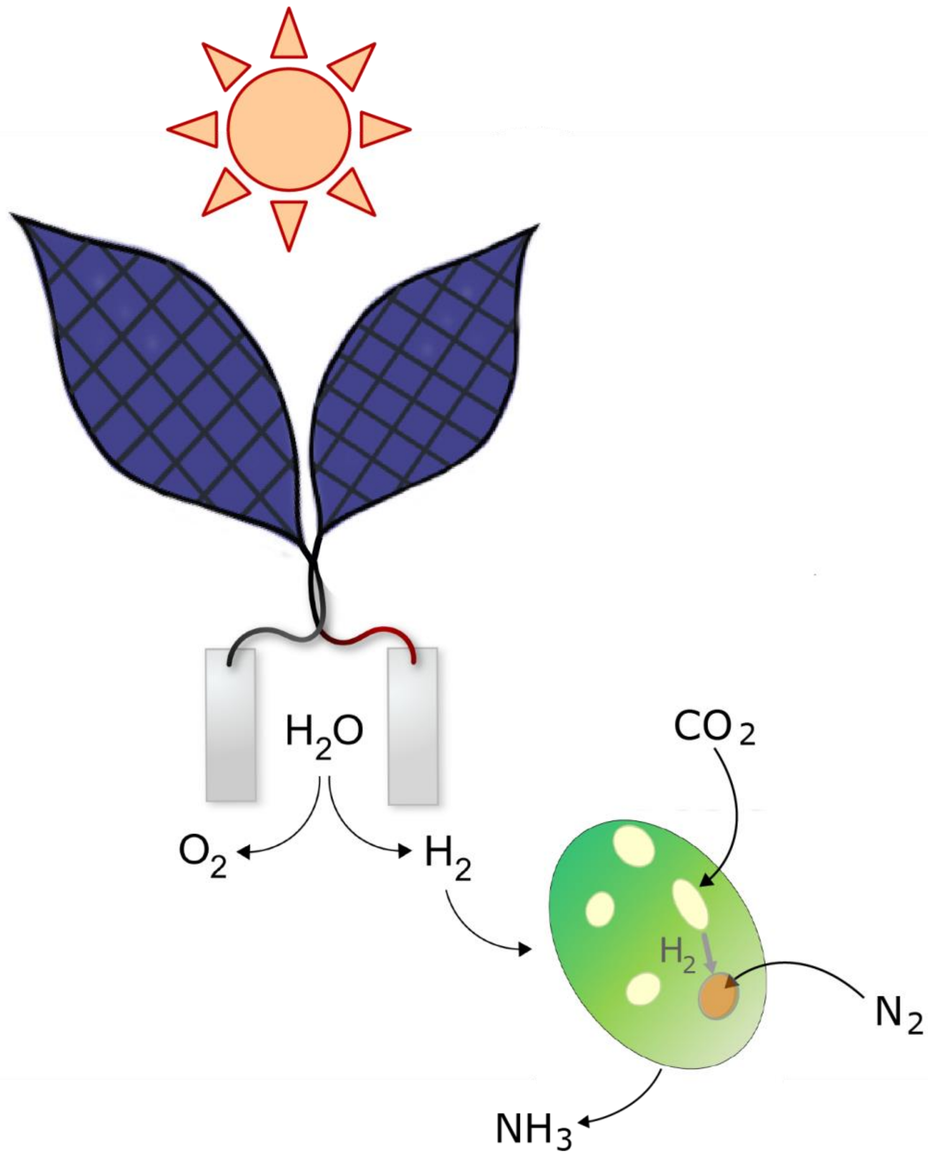
Nitrogen Fixation Important as an Energy and Food Target

$$N_2(g) + 1.5CH_4 + 1.5O_2 \rightarrow 2NH_3(aq) + 1.5CO_2(g)$$

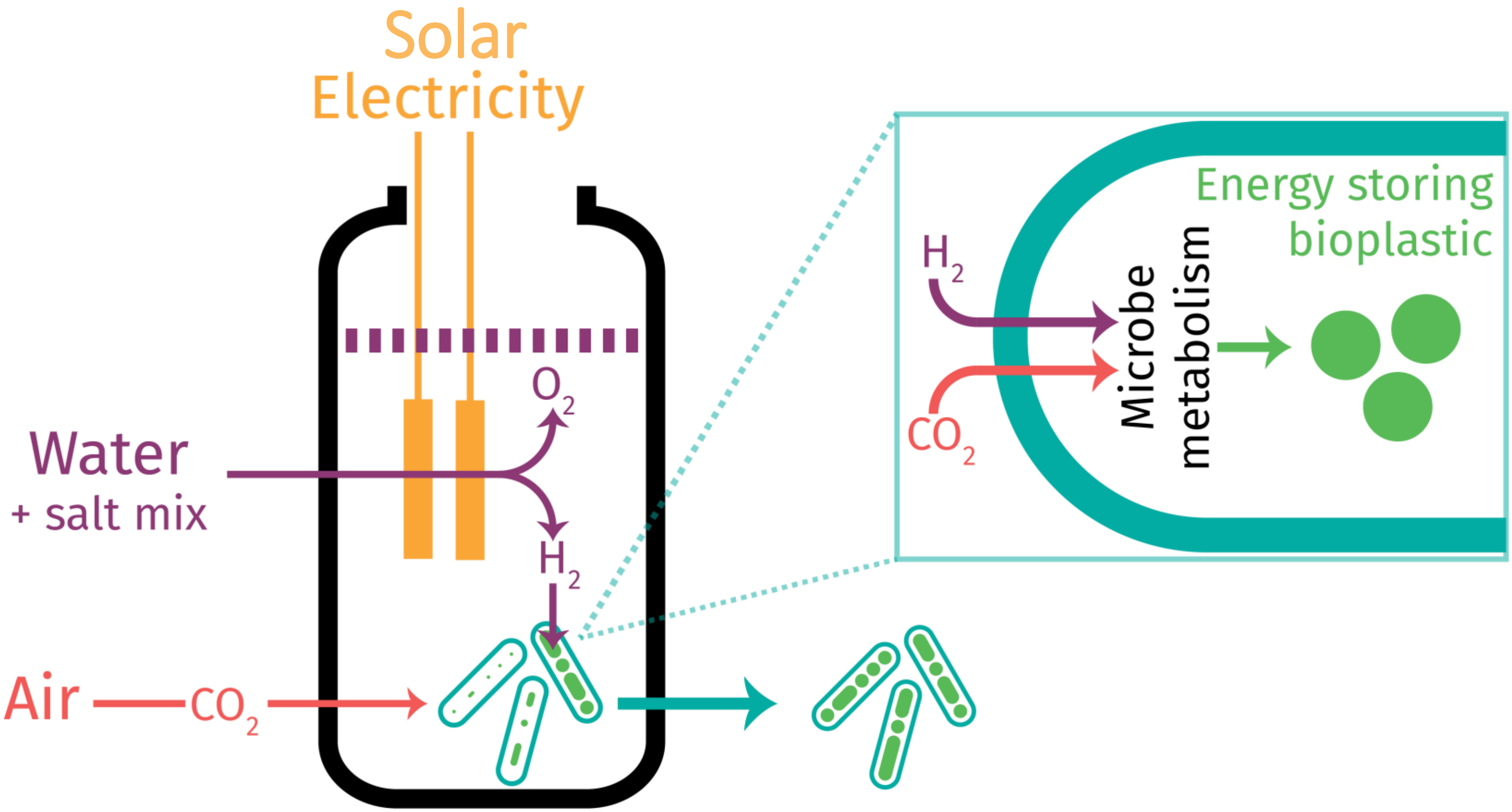
Haber-Bosch process:

- Energy intensive: 1~2% world energy supply
- High CO_2 emission: 3~5% world natural gas use

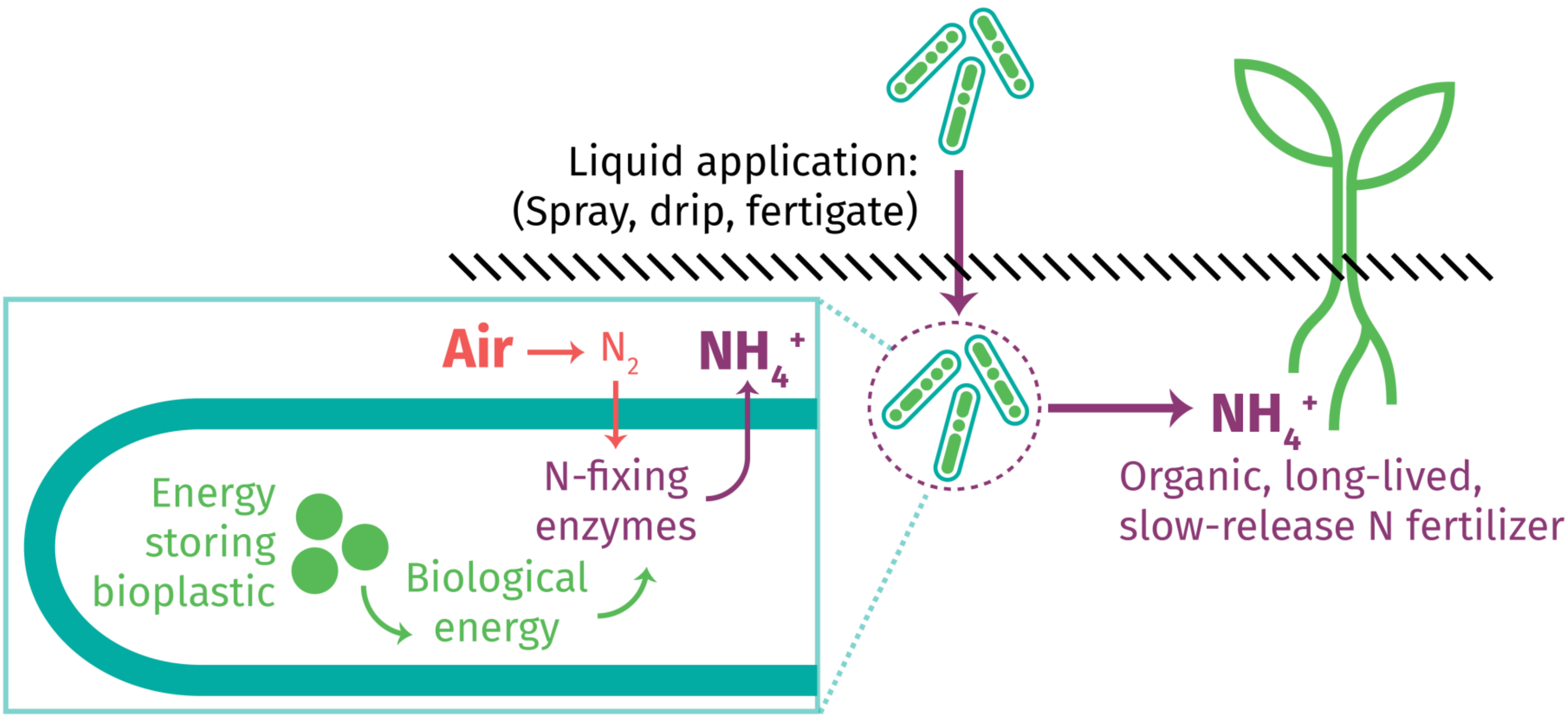
Bionic Leaf 2
(Water Splitting + Carbon/Nitrogen Fixing Organisms)



Steps 1 and 2: (1) Split Water and (2) Fix H_2 with CO_2 to Make Internal Cellular Energy Supply for Microbes



Step 3: Microbe Uses Stored Energy and Hydrogen to Make Ammonia

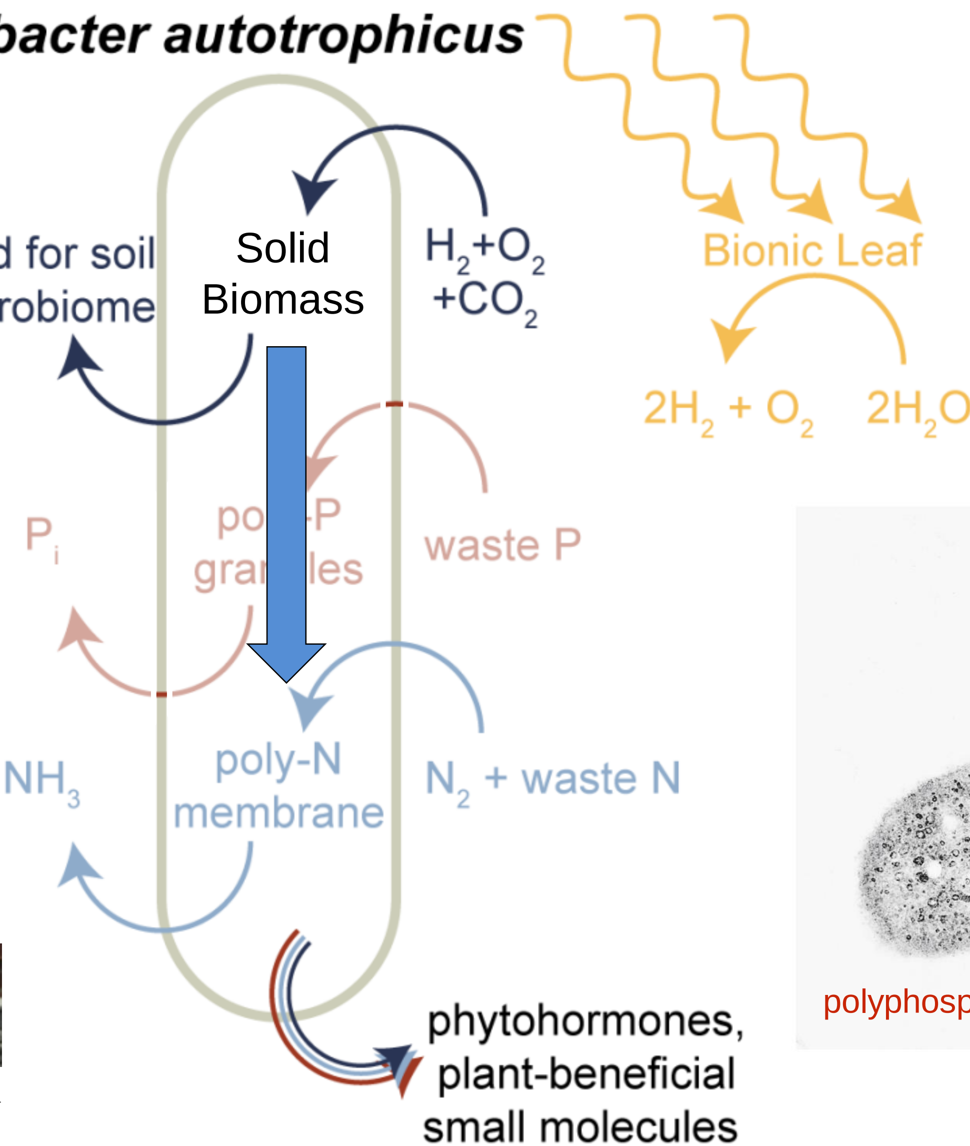


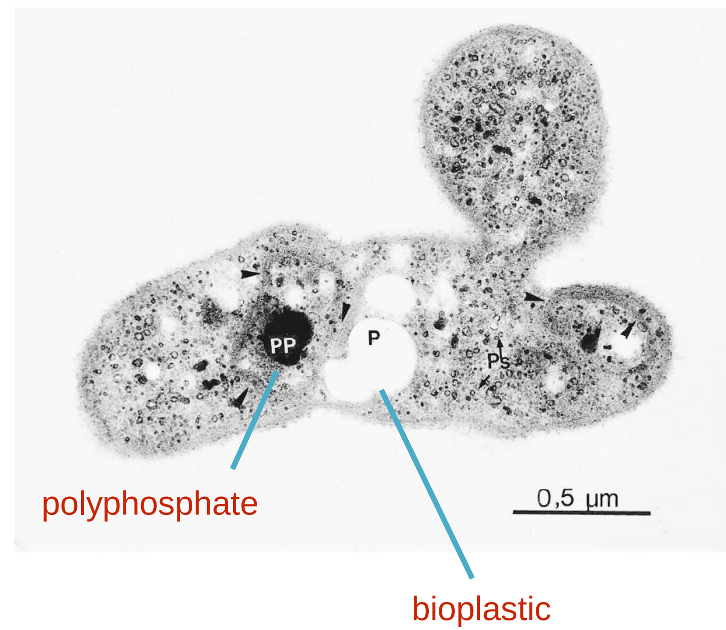
Nitrogen fixation is an energy intensive process:

$$N_2 + 8H^+ + 16ATP + 8e^- \rightarrow 2NH_3 + H_2 + 16ADP + 16P_i$$

This approach circumvents down regulation

A Living Biofertilizer

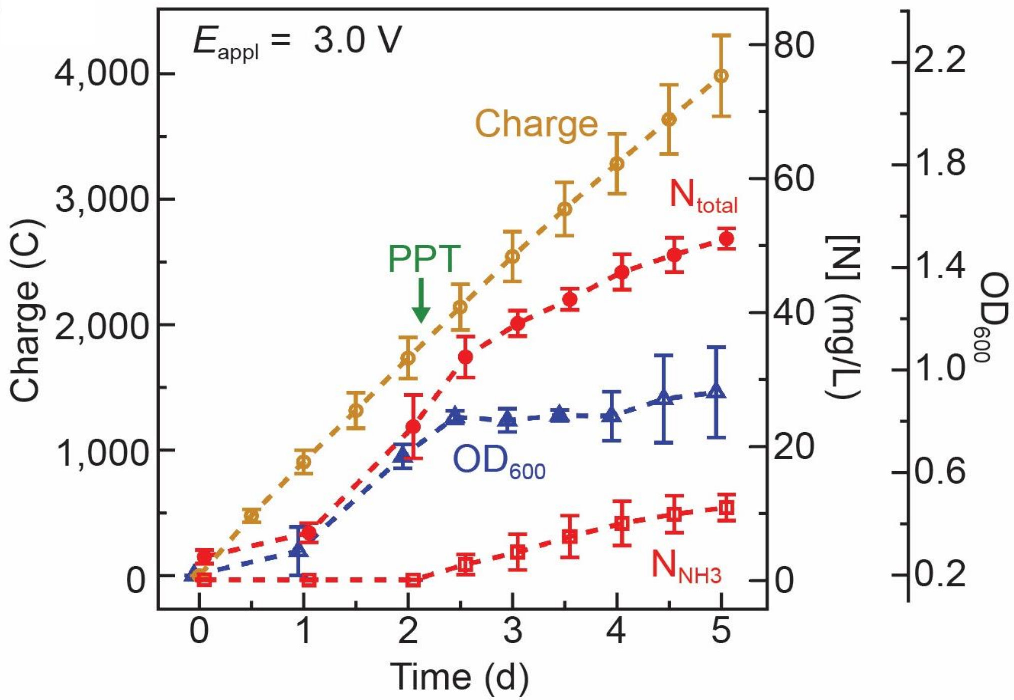


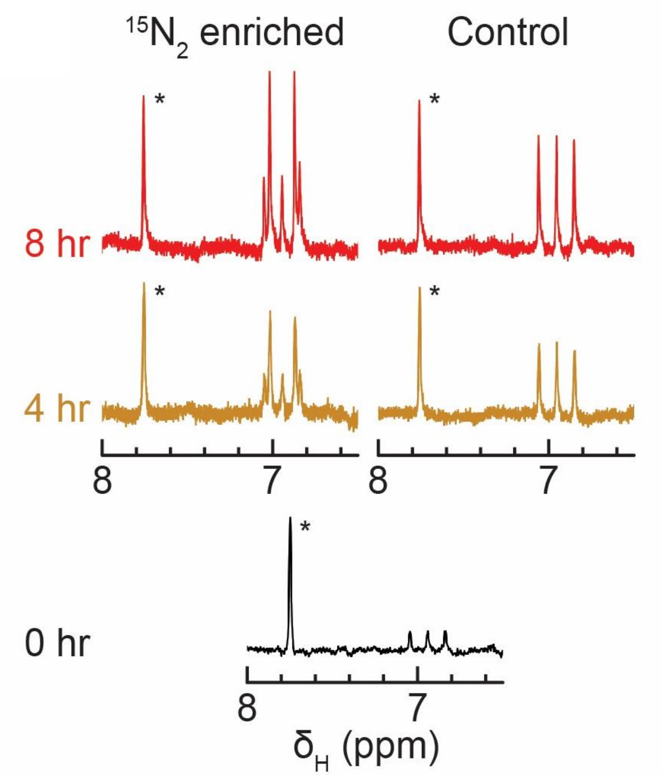


Kelsey Sakimoto
Kula Bio

Chong Liu
Asst Prof
UCLA

Microbes Exposed to ^{15}N-Enriched N_2 after PPT Addition





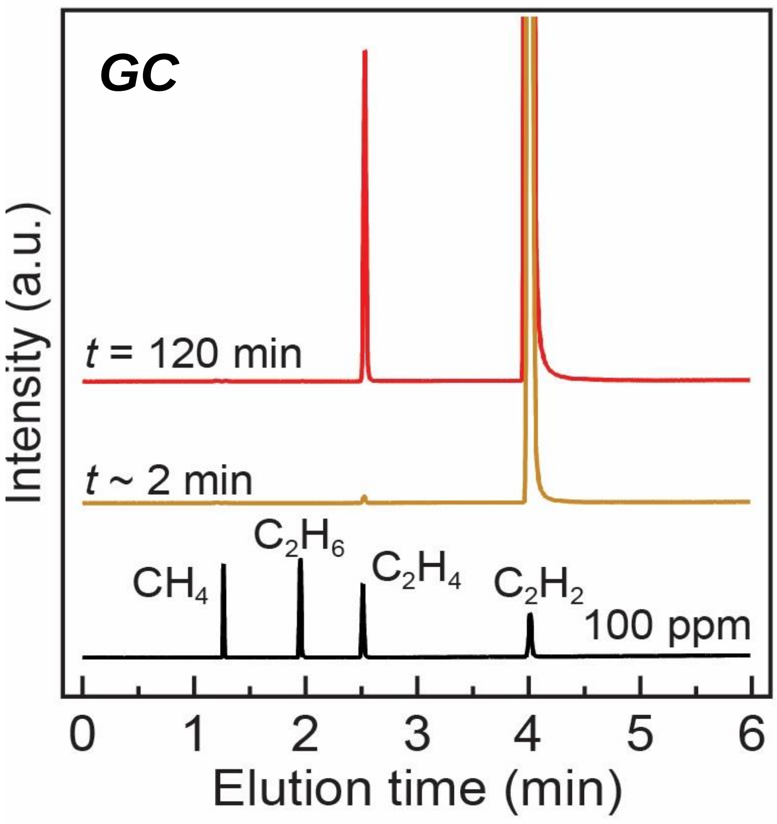
$H{-}^{14}NH_3^+$: t, 6.95 ppm. $J^1_{NH} = 50.0$ Hz

$H{-}^{15}NH_3^+$: d, 6.91 ppm. $J^1_{NH} = 72.7$ Hz

* $H{-}CON(CH_3)_2$ as internal standard

Can Determine TOF and TON from Acetylene Reduction

$$N_2 + 8H^+ + 16ATP + 8e^- \rightarrow 2NH_3 + H_2 + 16ADP + 16P_i$$



C_2H_2 reduction into C_2H_4:

127 ± 33 μM $C_2H_2 \cdot h^{-1}$

$\sim$12 mg/L N_{total} per day

1.0 OD_{600}:

2.8×10^8 mL^{-1} (flow cytometry)

TON:

3.1×10^9 per cell (5-d)

$TOF = 1.4 \times 10^4\ s^{-1}$ per cell

5000 MoFe protein per cell
(*Eur. J. Biochem*, 1995)

$\sim 3\ s^{-1}$ per MoFe protein

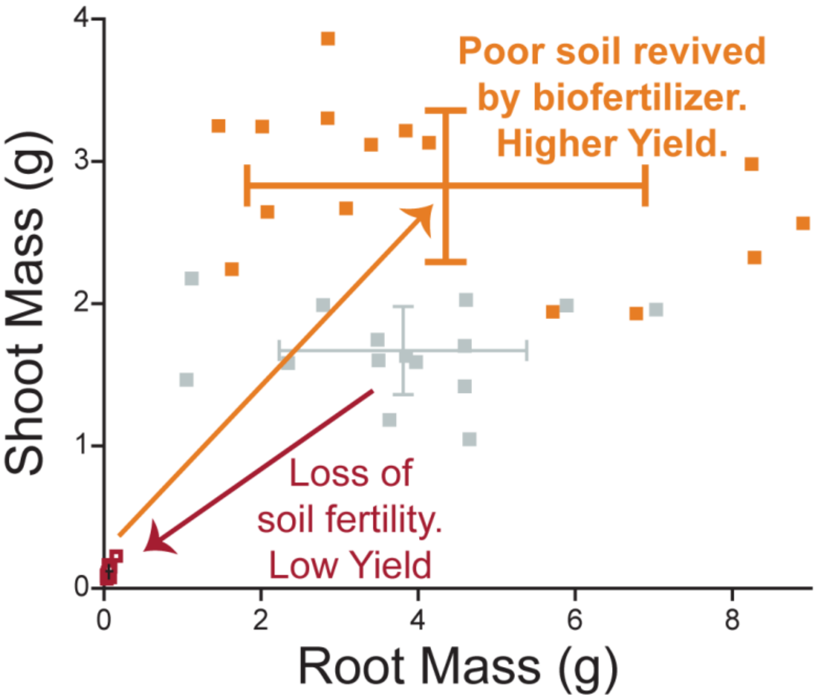
A Living Biofertilizer

no biofertilizer

w/ biofertilizer

- **~150%** increase in radish (model crop) yield with biofertilizer

- Biofertilizer **revitalizes degraded soil**, restores soil fertility and biological activity for better plant growth
- Reverses damage to agricultural soils



Lettuce and Sweet Corn (Midseason)

No Fertilizer

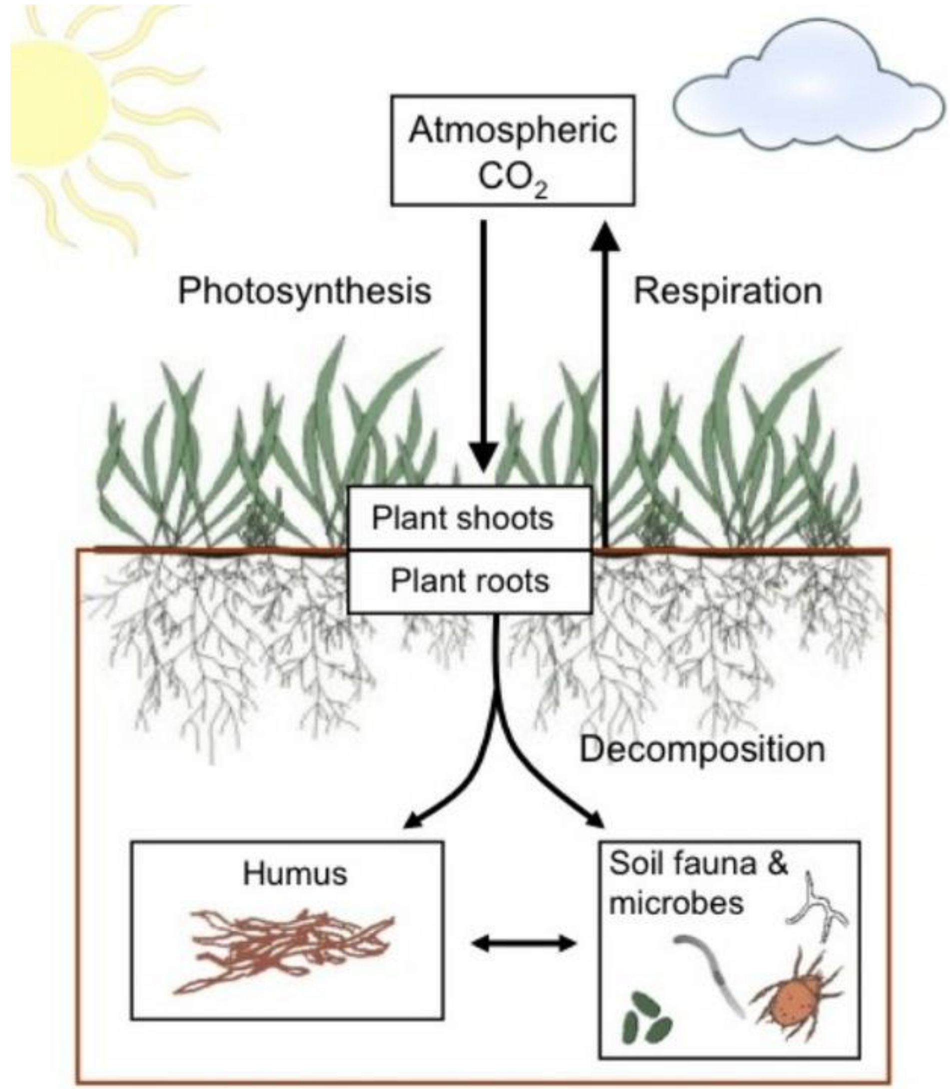
Synthetic
100% Urea-Ammonium-Nitrate

KM8
50% UAN + 50% KM8

Estimated KM8 delivers at least **60-65 lb N/acre**

A Carbon Negative Fertilizer

- **Carbon neutral:** Producing synthetic N-fertilizer **emits 245 million tons CO_2/year**
- **Carbon negative:** This is **a CO_2-negative** fertilizer … after H_2 withdrawn from PHB, carbon left behind in soil



Average US Farm: Sequester 16K lb CO_2
Eliminate 125K lb CO_2

KM8 sequesters 16,000 lb CO_2

KM8 CO_2 sequestration per lb N
–0.614 lb CO_2 / lb N

Total annual farm N demand
26,000 lb N / year

1 farm = –16,000 lb
using KM8 sequestered CO_2

H-Bosch emits 109,000 lb CO_2

H-Bosch CO_2 emissions per lb N
+4.2 lb CO_2 / lb N

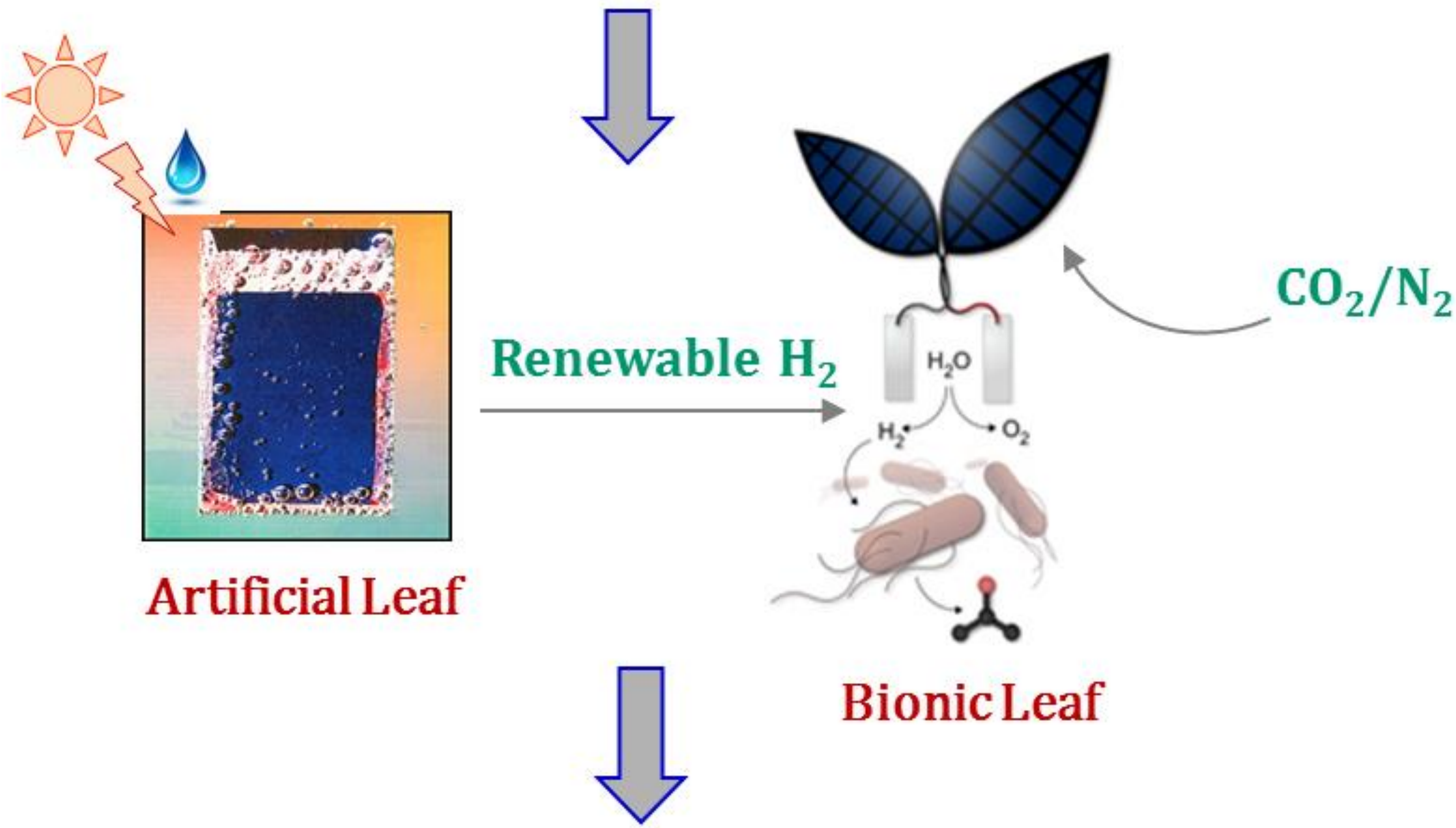
Total annual farm N demand
26,000 lb N / year

1 farm = 109,000 lb
using Haber-Bosch emitted CO_2

runoff & NO_x

Note: Assumes 400 acre farm with 65 lb/acre N demand for 26,000 lb N farm demand

Sunlight + Air + Any Water



Distributed Fuel (C neutral) and P|N Fertilizer (C negative)

Negative carbon budget my be large when high efficiency carbon fixation (i.e., fast biomass) is interfaced to agriculture

With Much Gratitude

All funding for this project provided by a 4-yr gift from ….

Kat Taylor

Tom Steyer