Artificial Leaf and Bionic Leaf

Fuel and Food: Sunlight, Air and (Any) Water
Photosynthesis is a Two-Step Process

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + \text{"2H}_2" + \text{NADPH} \]

\[ \text{"2H}_2" + \text{CO}_2 \rightarrow \text{biomass} \]
Two Step Process to Achieve Complete Artificial Photosynthesis

\[ 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- \quad \text{(CH}_2\text{O})_n \]

Energy storage

Solar \( h_v \)

Energy out

Hydrogen storage

\[ \text{CO}_2 \]

\[ \text{CO}_2 \]
Thermodynamics of Fuel Formation

$$G^o = -nF E^o$$

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

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

CO$_2$ reduction with hydrogen to fuels is thermoneutral:

$$\text{CO}_2 + 6H^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^o = 0.17 \text{ V}$$
$$\text{CO}_2 + 8H^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^o = 0.03 \text{ V}$$
$$3\text{CO}_2 + 18H^+ + 18e^- \rightarrow i-\text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O} \quad E^o = 0.09 \text{ V}$$
$$4\text{CO}_2 + 24H^+ + 24e^- \rightarrow i-\text{C}_4\text{H}_9\text{OH} + 7\text{H}_2\text{O} \quad E^o = 0.11 \text{ V}$$
$$5\text{CO}_2 + 30H^+ + 30e^- \rightarrow i-\text{C}_5\text{H}_{11}\text{OH} + 9\text{H}_2\text{O} \quad E^o = 0.08 \text{ V}$$

The Light Reaction

\[ 2H_2O \rightarrow O_2 + "2H_2" + \text{NADPH} \]

\[ "2H_2" + \text{CO}_2 \rightarrow \text{biomass} \]

day

night
Self Healing Water Splitting

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e^- + 4\text{H}^+ \]

Co phosphate oxide

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

OER catalyst

Co-OEC

ITO

Tunnel junction

p

i: a-Si

Tunnel junction

n

i: a-SiGe

Zinc oxide

Metal reflector

Stainless steel

HER catalyst

NiMoZn

O₂

H₂

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

"2H₂" + CO₂

biomass

day

night

2H₂O

O₂ + "2H₂"

NADPH
Photosynthetic Membrane
PS I and PSII Replaced with the Artificial Leaf
Bionic Leaf 1
(Water Splitting + Carbon Fixing Organisms)
Natural Photosynthesis → All Artificial Photosynthesis

**Photosynthesis**
- Chloroplast
- PSII ➔ PSI ➔ e- transport chain ➔ 2 NADPH ➔ 2 NADP+
- Atmospheric CO₂ ➔ Calvin Cycle ➔ GAP ➔ Biomass ➔ Natural Metabolism ➔ GAP

**Replace PS**
- Ralstonia eutropha
- H₂ase ➔ H₂ ➔ 2 NADPH ➔ 2 NADP+
- Atmospheric CO₂ ➔ Calvin Cycle ➔ GAP ➔ Engineered Metabolism ➔ GAP ➔ Transporter ➔ Sugars, Fuels, Chemicals

**Renewable H₂**
- Anode ➔ PV ➔ H₂ ➔ 2H₂O ➔ 4H⁺ + O₂
- Renewable H₂ ➔ 2NADPH ➔ 2NADP+
- Ralstonia eutropha
- Engineered Metabolism ➔ GAP ➔ Transporter ➔ Sugars, Fuels, Chemicals

GAP = glyceraldehyde-3-phosphate
Re-engineered *R. eutropha* for Isopropanol Production

wt *R. eutropha* converts acetyl-CoA to biomass and polyhydroxybutyrate (PHB).

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Brendan Colón
Amazon
Energy Efficiency Calculation

\[ \eta_{elec} = \frac{\Delta_r G^0 \times N}{C \times E_{appl}} \]

- Gibbs free energy of CDR \( \times \) moles of product
- Electric energy input for \( \text{H}_2 \) production
- Charge passed \( \times \) voltage for water splitting

For isobutanol:

\[ 4\text{CO}_2(g) + 5\text{H}_2\text{O}(l) \rightarrow \text{C}_4\text{H}_{10}\text{O}(l) + 6\text{O}_2(g) \]

<table>
<thead>
<tr>
<th>( \Delta_r G^0 ) (kJ mol(^{-1}))</th>
<th>N (mol)</th>
<th>( \Delta_r G ) (kJ)</th>
<th>C (Coul.)</th>
<th>( E_{appl} ) (V)</th>
<th>C ( \times E ) (kJ)</th>
<th>( \eta_{elec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1951</td>
<td>( 8.98 \times 10^6 )</td>
<td>1.56</td>
<td>2510</td>
<td>2.0</td>
<td>5.02</td>
<td>31%</td>
</tr>
</tbody>
</table>

For an 20% PV, 6.0% SFE
Bionic Leaf is Ten Times Better than Natural Photosynthesis

The diagram shows a comparison of solar efficiency ($\eta_{\text{solar}}$) for various categories:

- **Biomass**
- **PHB**
- **C$_{3\text{ol}}$**
- **C$_{4\text{+C}_{5\text{ols}}}$**

The categories are compared against:

- **microalgae**
- **best crops**
- **starches/sugars**

The efficiency values are indicated, with error bars showing the variability in the data.
C10+ Fuels

4 C initially, then add 2 C at a time

Central Metabolism

Initial Condensation

Initial Condensation

medium chain FA selectivity by altering thioesterase

Fatty acid chain length

Fatty acid chain length
Nitrogen: Another Biogenic Element in Air
Nitrogen Fixation Important as an Energy and Food Target

\[ \text{N}_2(\text{g}) + 1.5\text{CH}_4 + 1.5\text{O}_2 \rightarrow 2\text{NH}_3(\text{aq}) + 1.5\text{CO}_2(\text{g}) \]

Haber-Bosch process:
• Energy intensive: 1~2% world energy supply
• High CO\textsubscript{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 H₂ with CO₂ 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

**Xanthobacter autotrophicus**

- **P**
  - food for soil microbiome
  - Solid Biomass
  - $\text{H}_2 + \text{O}_2 + \text{CO}_2$
  - Bionic Leaf
  - $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

- **PP**
  - $\text{P}_i$
  - poly-P granules
  - waste P
  - $\text{NH}_3$
  - poly-N membrane
  - $\text{N}_2 + $ waste N
  - phytohormones, plant-beneficial small molecules

Kelsey Sakimoto, Kula Bio
Chong Liu, Asst Prof, UCLA

[Diagram showing the process involving Xanthobacter autotrophicus and its interactions with soil microbiome, solid biomass, and bionic leaf.]
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

\[
\text{N}_2 + 8\text{H}^+ + 16\text{ATP} + 8\text{e}^- \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{ADP} + 16\text{P}_i
\]

\[C_2\text{H}_2 \text{ reduction into } C_2\text{H}_4:\]
\[127 \pm 33 \text{ µM C}_2\text{H}_2 \cdot \text{h}^{-1}\]
\[\sim 12 \text{ mg/L N}_{\text{total}} \text{ per day}\]

\[1.0 \text{ OD}_{600}:\]
\[2.8 \times 10^8 \text{ mL}^{-1} \text{ (flow cytometry)}\]

\[\text{TON:}\]
\[3.1 \times 10^9 \text{ per cell (5-d)}\]

\[TOF = 1.4 \times 10^4 \text{ s}^{-1} \text{ per cell}\]
\[5000 \text{ MoFe protein per cell}\]
\[(\text{Eur. J. Biochem, 1995})\]
\[\sim 3 \text{ s}^{-1} \text{ per MoFe protein}\]
A Living Biofertilizer

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

no biofertilizer  w/ 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)

<table>
<thead>
<tr>
<th>No Fertilizer</th>
<th>Synthetic</th>
<th>KM8</th>
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<tbody>
<tr>
<td></td>
<td>100% Urea-Ammonium-Nitrate</td>
<td>50% UAN + 50% KM8</td>
</tr>
</tbody>
</table>

Estimated KM8 delivers at least 60-65 lb N/acre
• **Carbon neutral:** Producing synthetic N-fertilizer **emits 245 million tons CO\textsubscript{2}/year**

• **Carbon negative:** This is a CO\textsubscript{2}-negative fertilizer ... after H\textsubscript{2} withdrawn from PHB, carbon left behind in soil
**Average US Farm: Sequester 16K lb CO₂**

**Eliminate 125K lb CO₂**

<table>
<thead>
<tr>
<th>KM8 sequesters 16,000 lb CO₂</th>
<th>H-Bosch emits 109,000 lb CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>KM8 CO₂ sequestration per lb N</td>
<td>H-Bosch CO₂ emissions per lb N</td>
</tr>
<tr>
<td>-0.614 lb CO₂ / lb N</td>
<td>+4.2 lb CO₂ / lb N</td>
</tr>
<tr>
<td>Total annual farm N demand</td>
<td>Total annual farm N demand</td>
</tr>
<tr>
<td>26,000 lb N / year</td>
<td>26,000 lb N / year</td>
</tr>
</tbody>
</table>

1 farm = -16,000 lb CO₂ sequestered using KM8

1 farm = 109,000 lb CO₂ emitted using Haber-Bosch

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 may 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