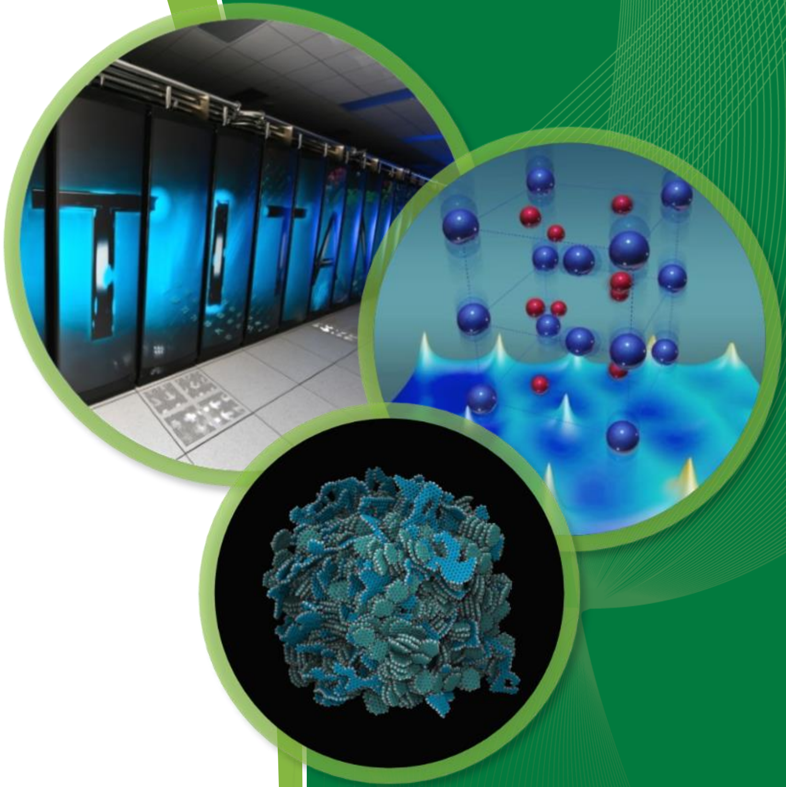
Nanotechnology Based Catalysts for the Electrochemical Synthesis of Low Carbon Fuel and Fertilizer



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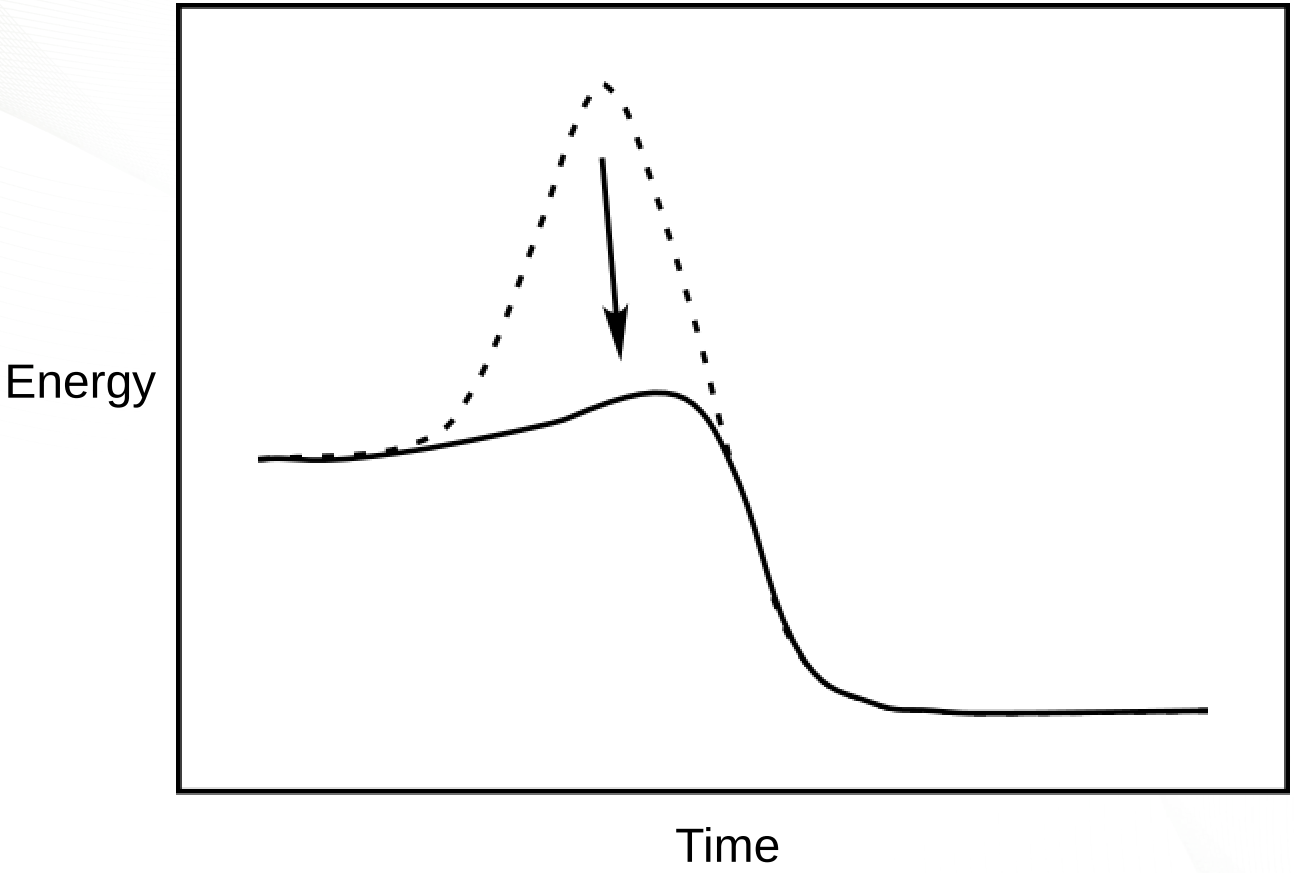
Oak Ridge National Laboratory

Outline

- Intro to catalysis and CO_2 chemistry
- Carbon nanospikes
- CO_2 conversion results
- Rough economic analysis

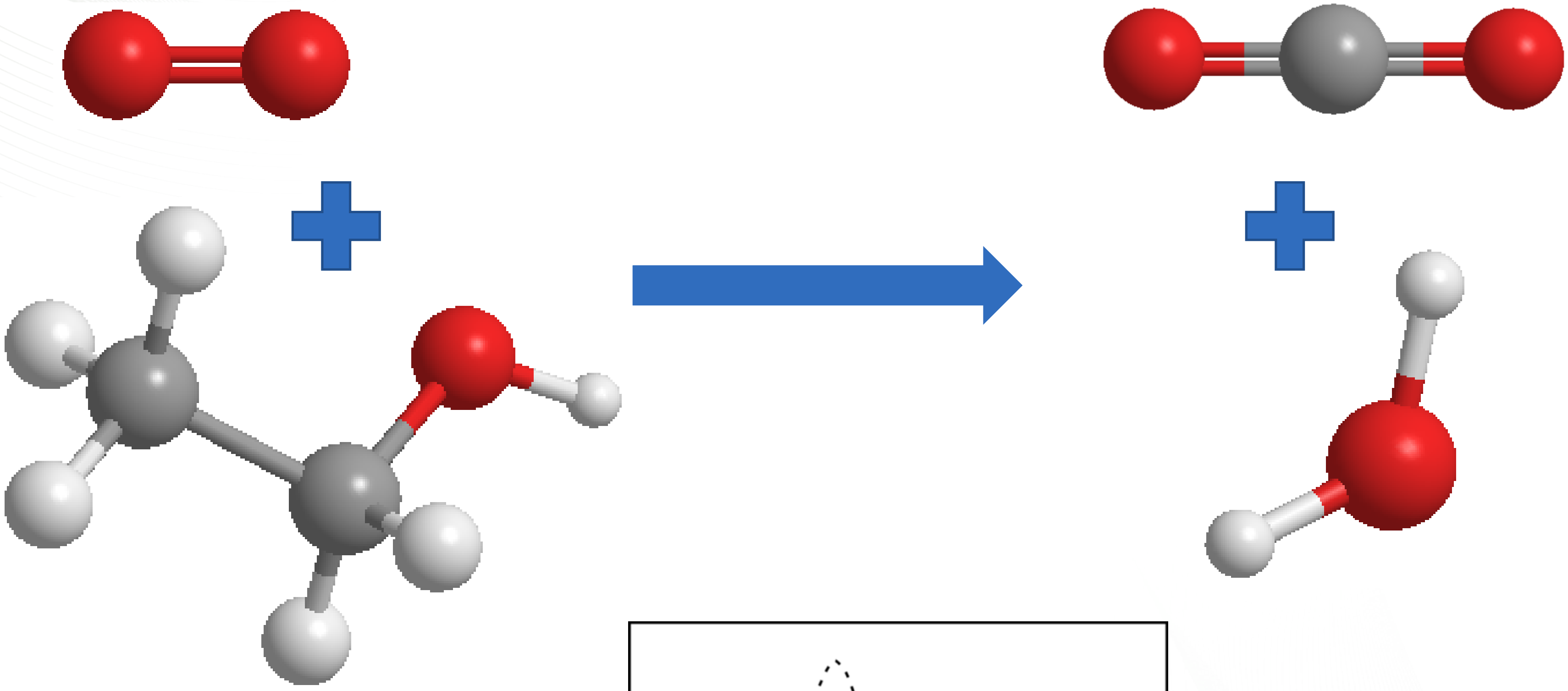
What is a Catalyst?

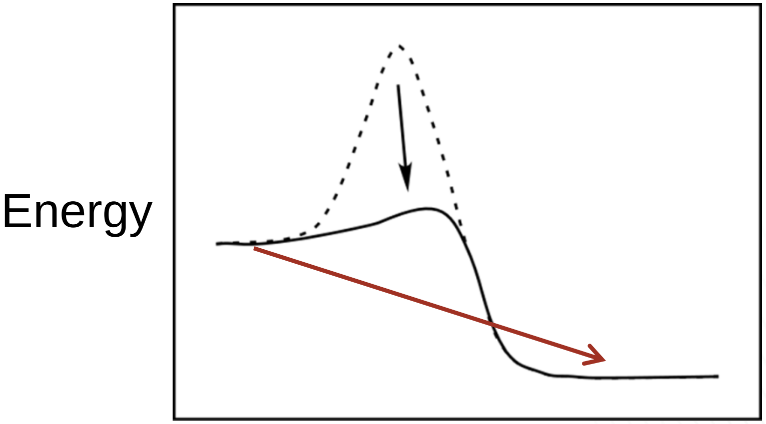


Some chemical reactions need energy to get started (e.g. combustion)
A catalyst lowers the energy needed for a chemical reaction

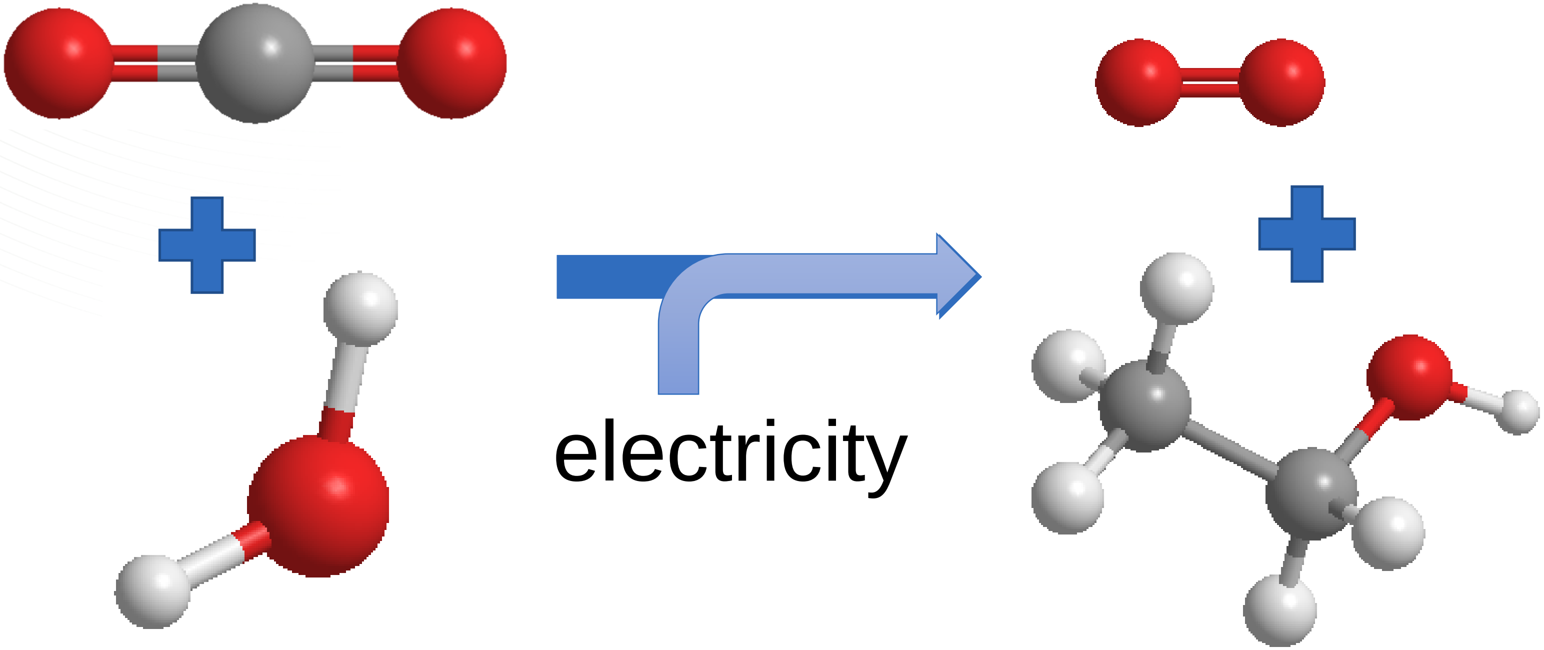
Catalytic converter combustion of carbon monoxide: $CO + O \rightarrow CO_2$

Carbon Dioxide and Combustion



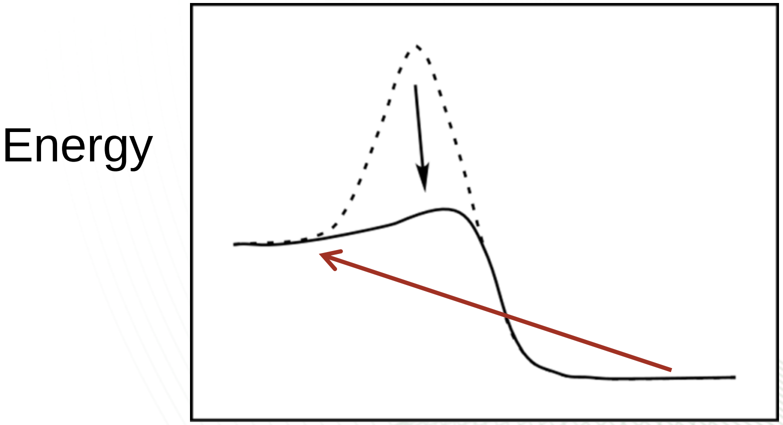


Converting Carbon Dioxide Back to Fuel

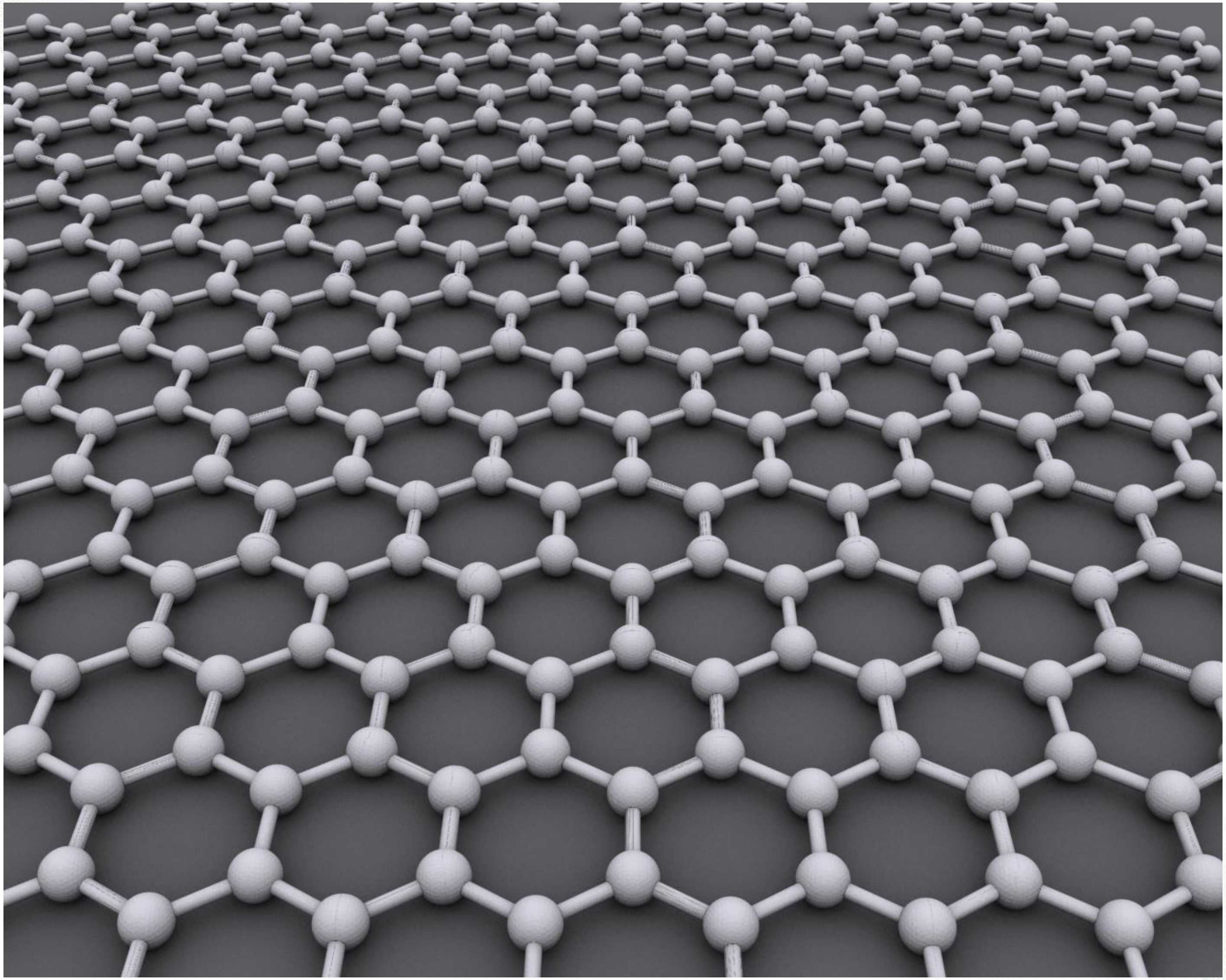


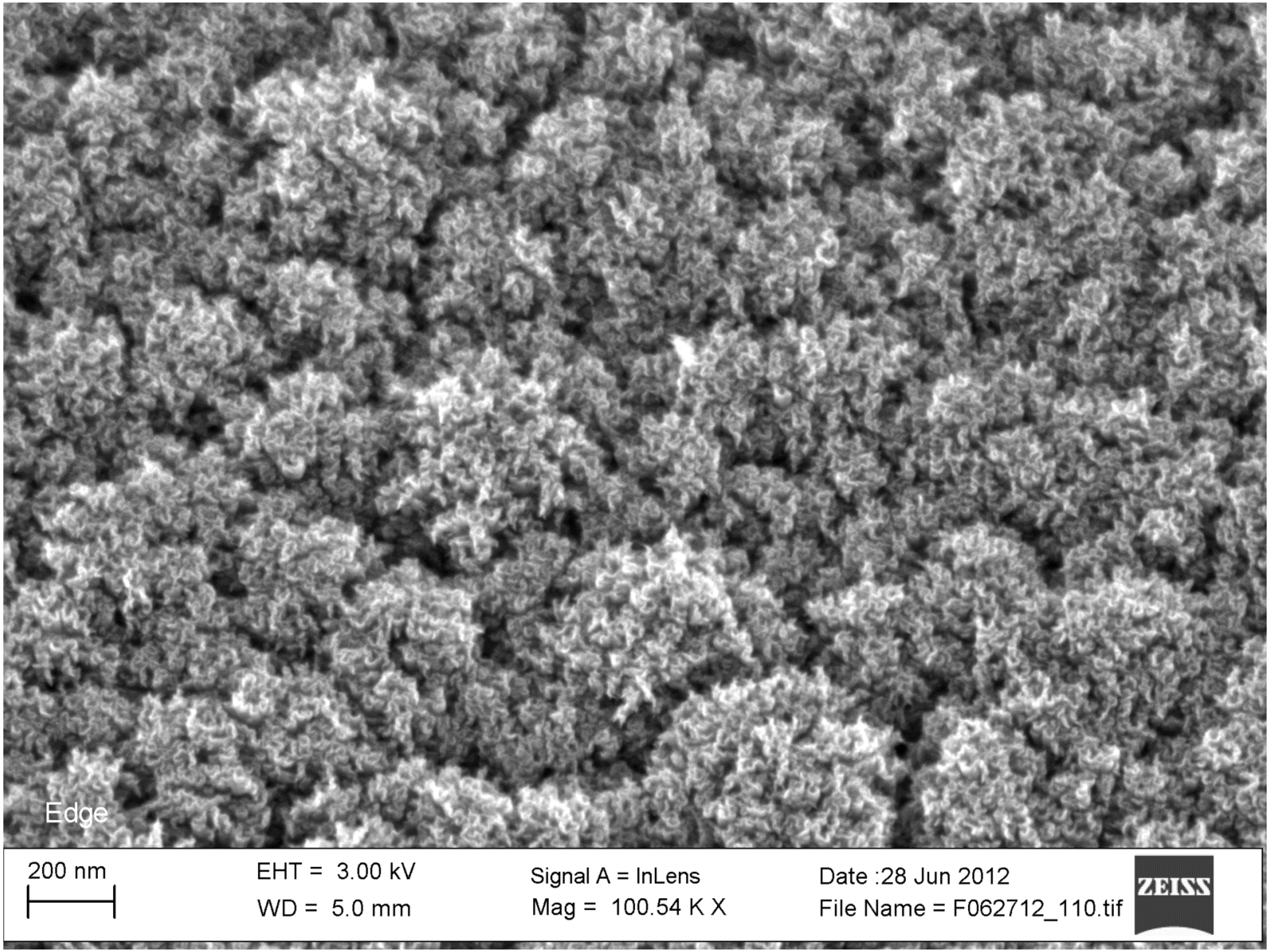
Due to rapid growth in renewable electricity generation demand is often poorly matched to supply

Electricity must be used as it is generated – no means to store on grid level



Graphene: Single Layer, Hexagonal Carbon

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Date :28 Jun 2012
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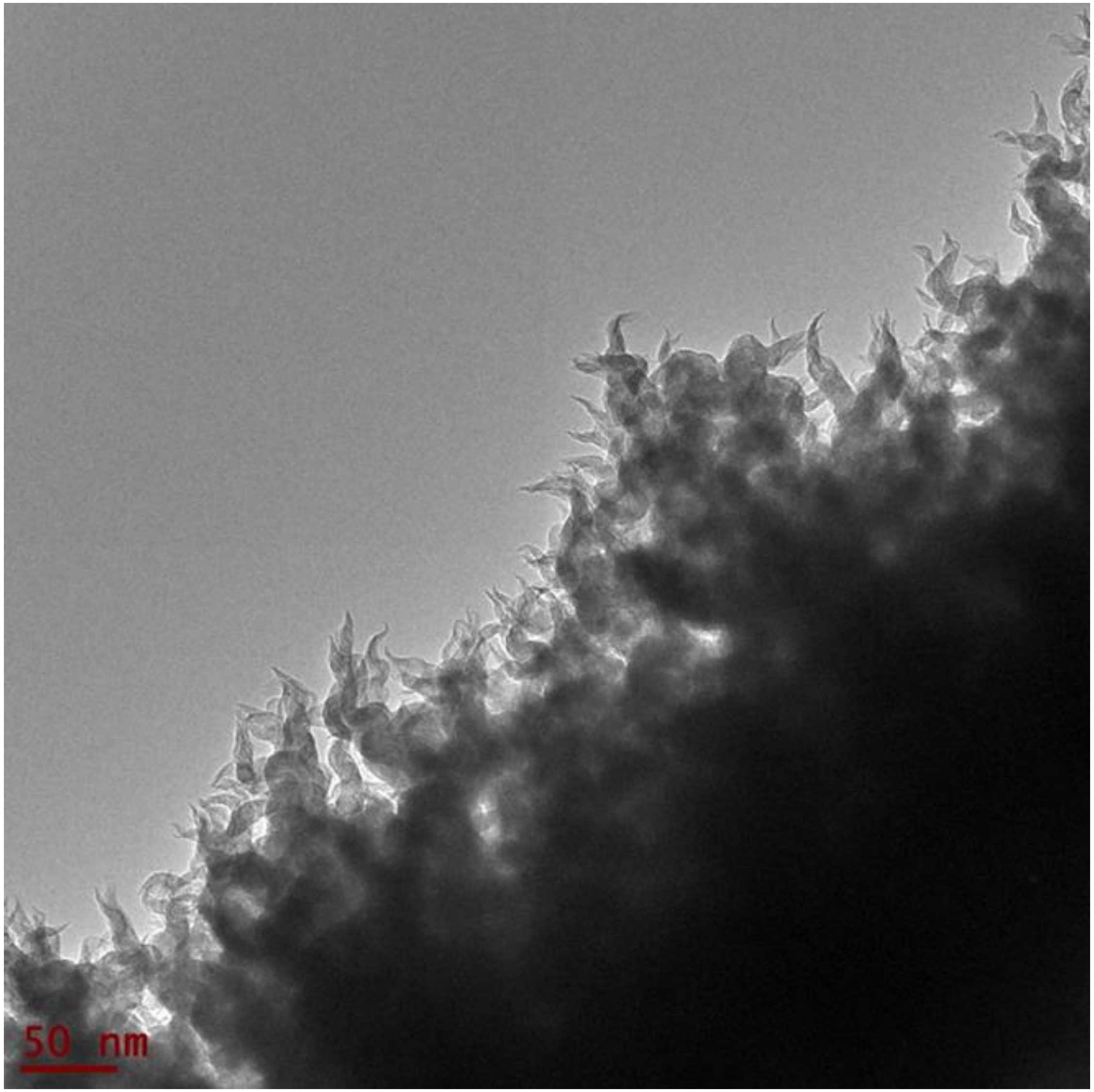
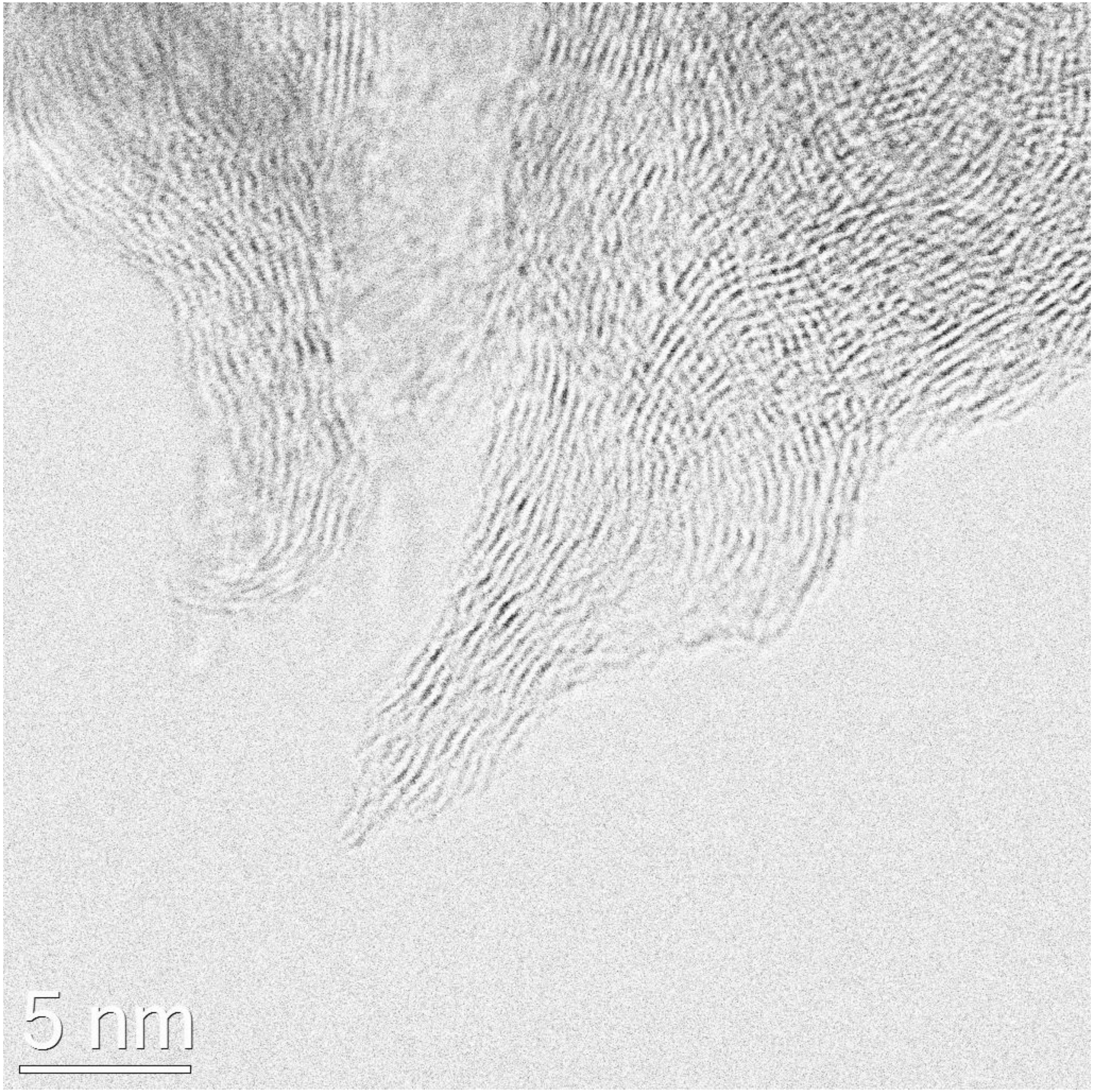
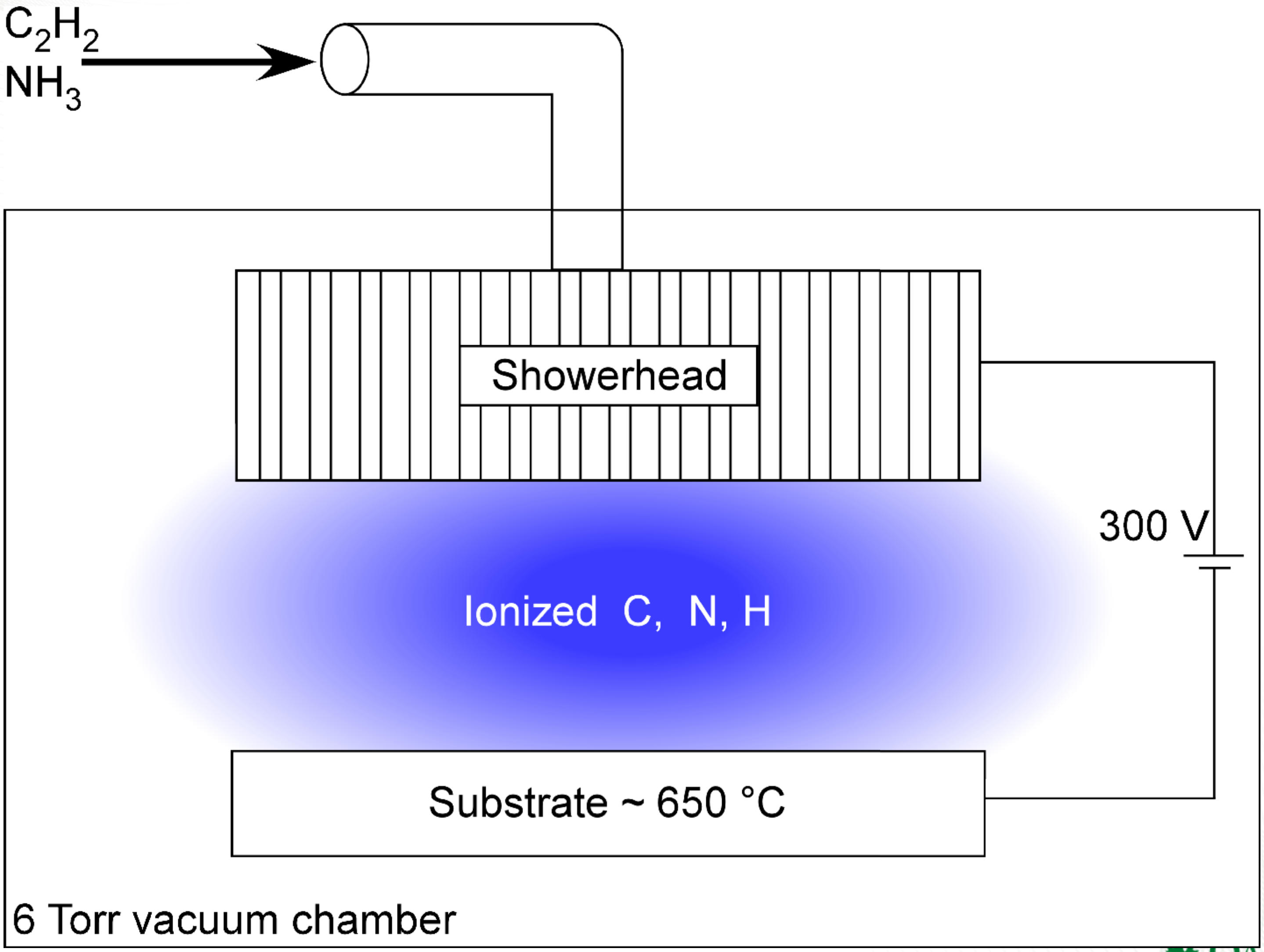
ZEISS

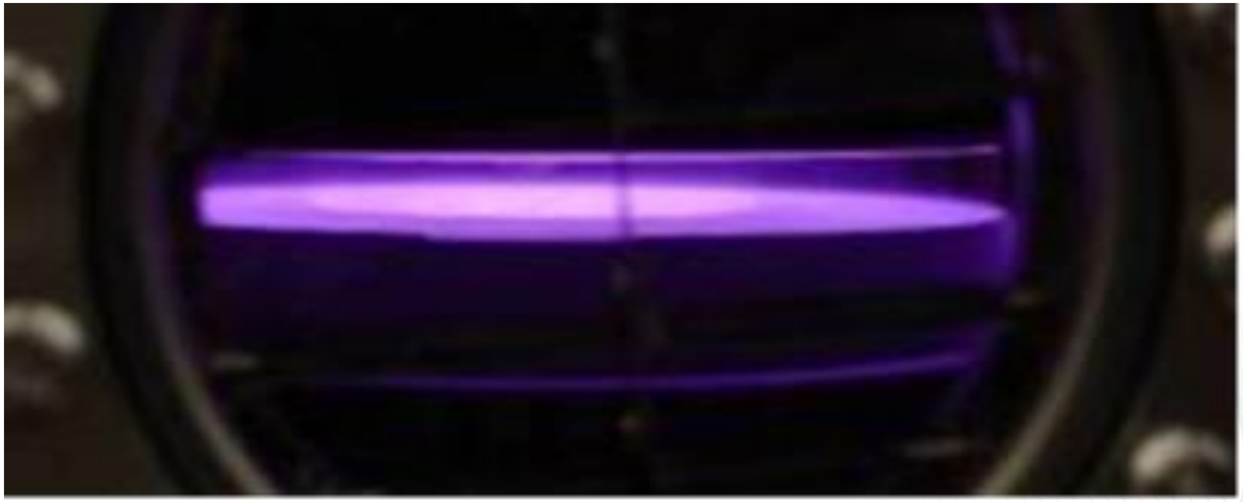

50 nm


5 nm

Plasma-Enhanced Chemical Vapor Deposition (PECVD)



Plasma-Enhanced Chemical Vapor Deposition



The Trion Minilock-Orion is a Plasma Enhanced Chemical Vapor Deposition system with a vacuum loadlock that produces production-quality films on a compact platform. By adding a loadlock, dopants can be used on the PECVD films. The unique reactor design produces low stress films with excellent step coverage at extremely low power levels.

The system meets all safety, facility and process requirements within the laboratory and pilot line production environments.

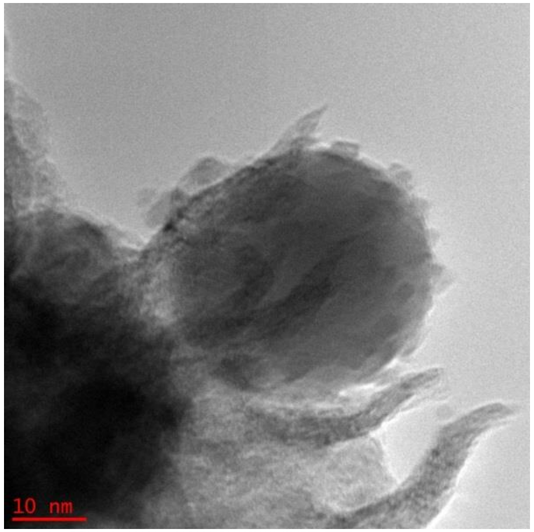
Applications:
MEMS, Solid State Lighting, Failure Analysis, Research & Development, Pilot Line

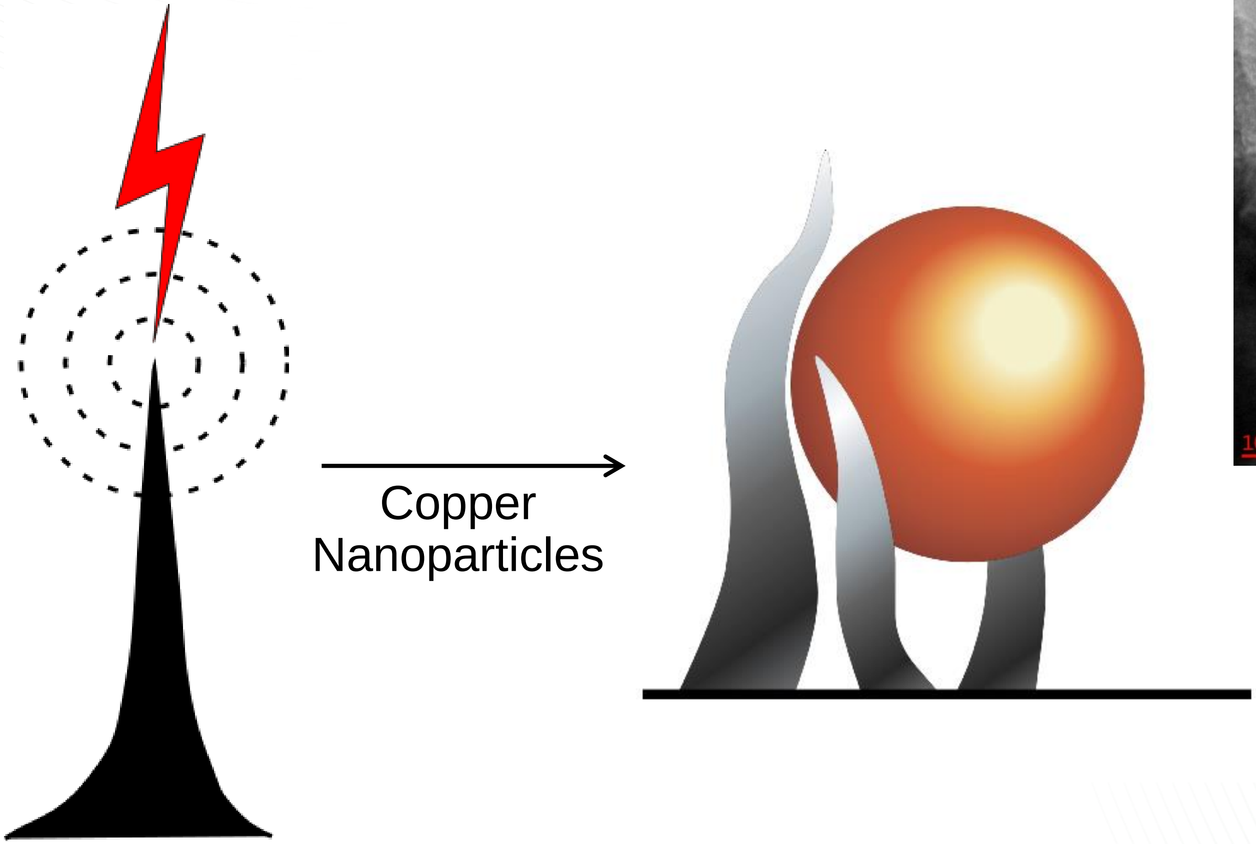
Process Gases: 100% Silane, Ammonia, TEOS, Diethylsilane, Nitrous Oxide, Oxygen, Nitrogen, Trimethylsilane, Methane

http://triontech.com/deposition-products/minilock-pecvd/ Contact: Sol Spencer (727) 461-1888

Carbon Nanospikes are Dense and Numerous

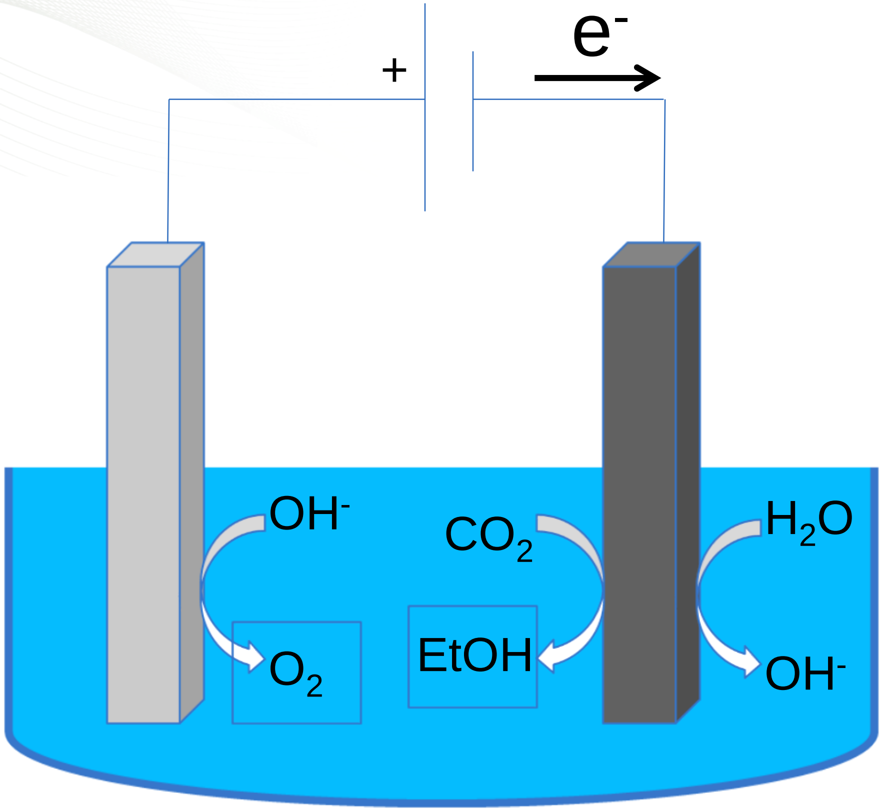
- Approximately 1x10^{13} spikes per sheet of copy paper
    - Roughly equivalent to the number of dollars in the national debt
- Each nanospike will concentrate electric field





Copper
Nanoparticles

Electrolysis ~ Charging a Battery



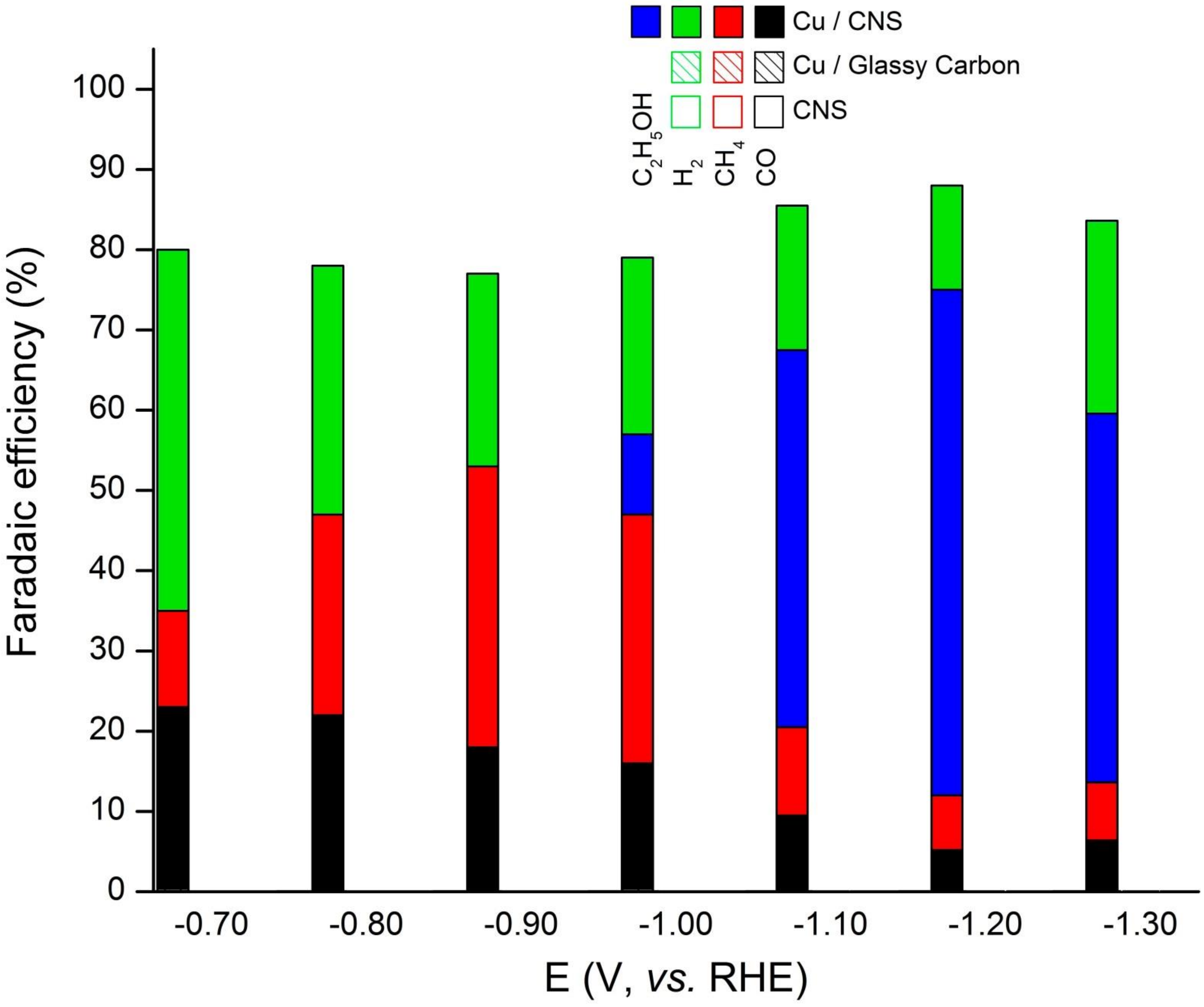
CABB Group GmbH

Cathode (catalyst) half-reaction: $9H_2O + 9e^- \rightarrow 9H + 9OH^-$

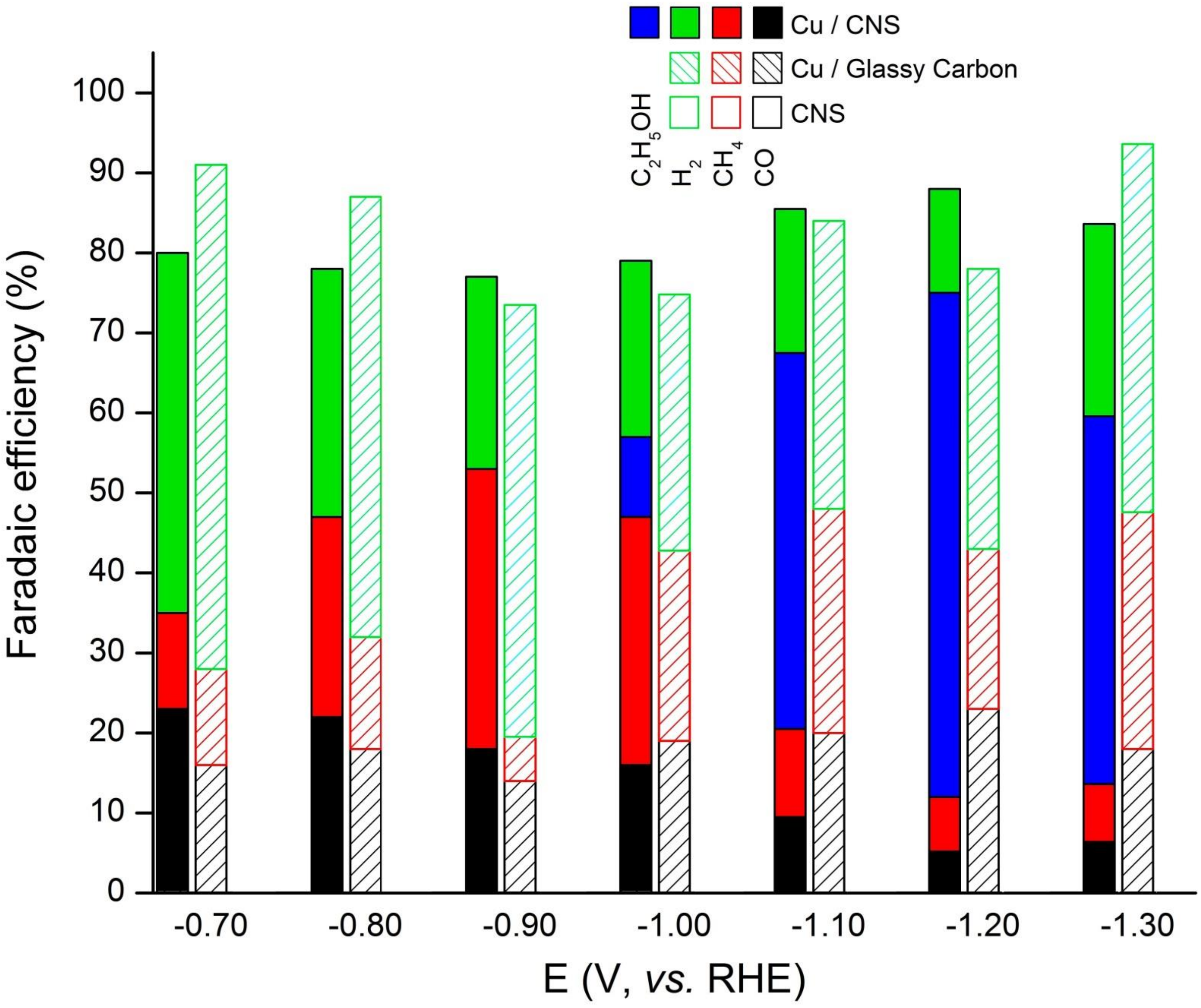
$2CO_2 + 9H + 3e^- \rightarrow C_2H_5OH + 3OH^-$

Anode half-reaction: $12OH- \rightarrow 3O_2 + 6H_2O + 12e^-$

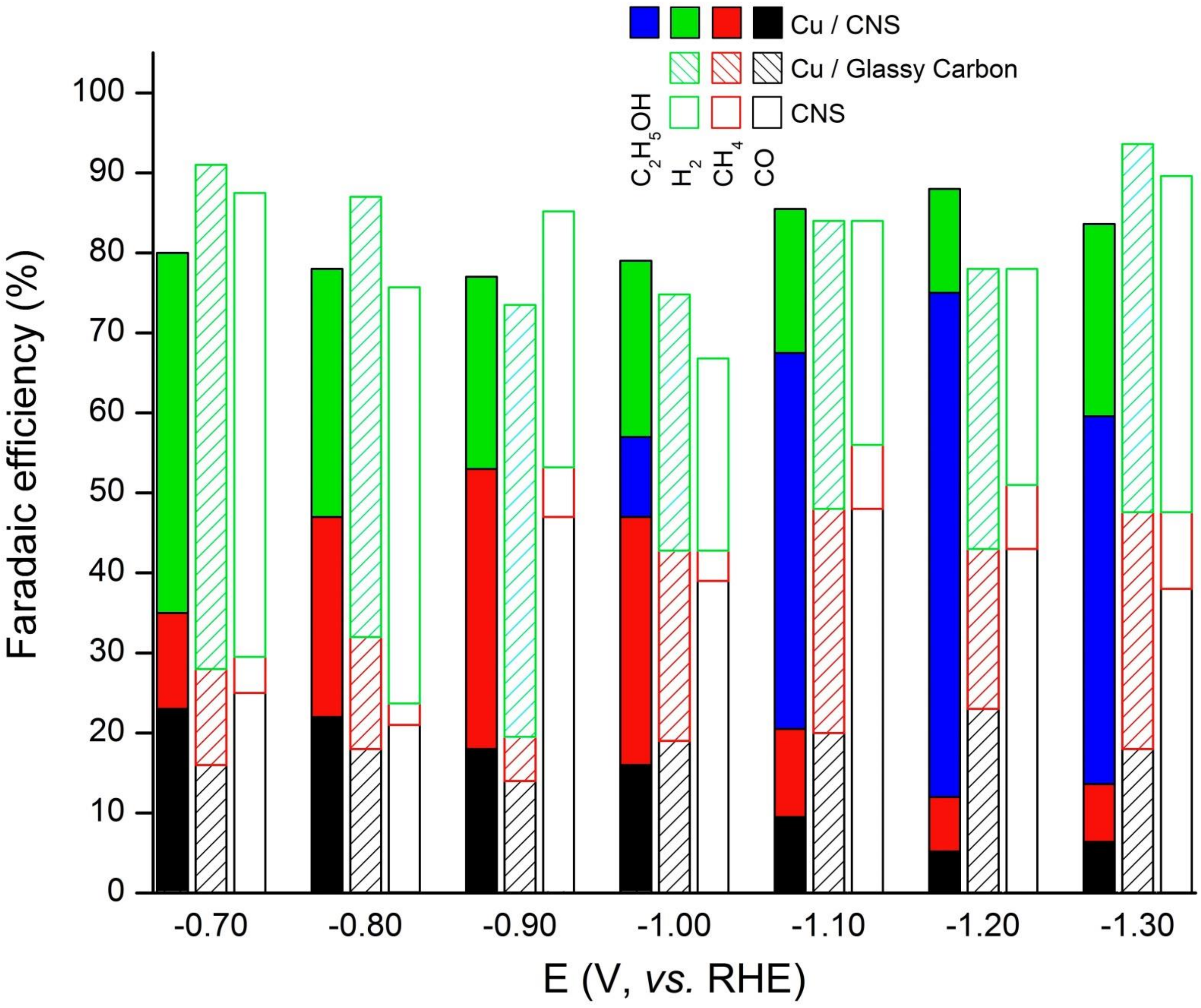
Result: Products from CO_2 Conversion



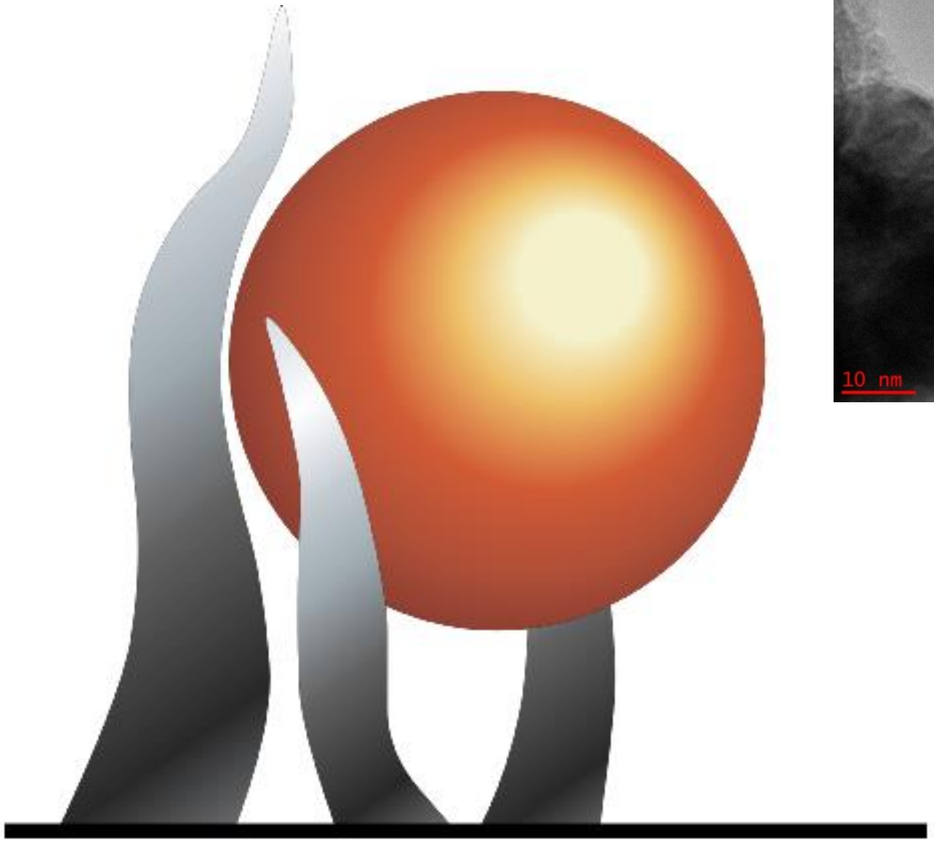
Result: Products from CO_2 Conversion

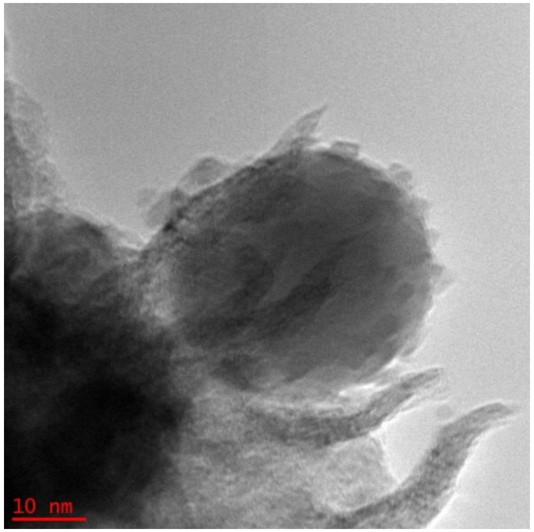


Result: Products from CO_2 Conversion

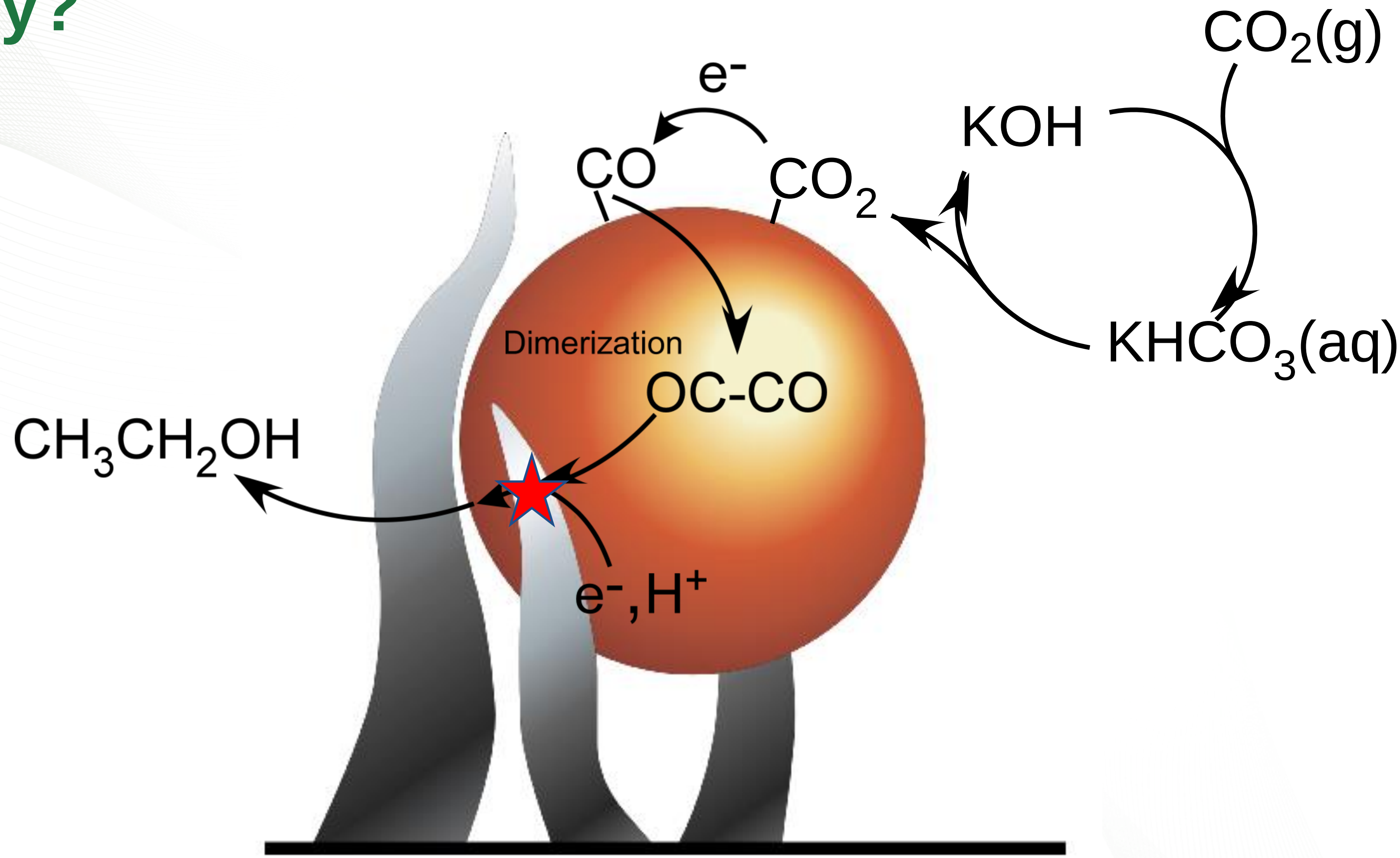


Why Mostly C2 Products?

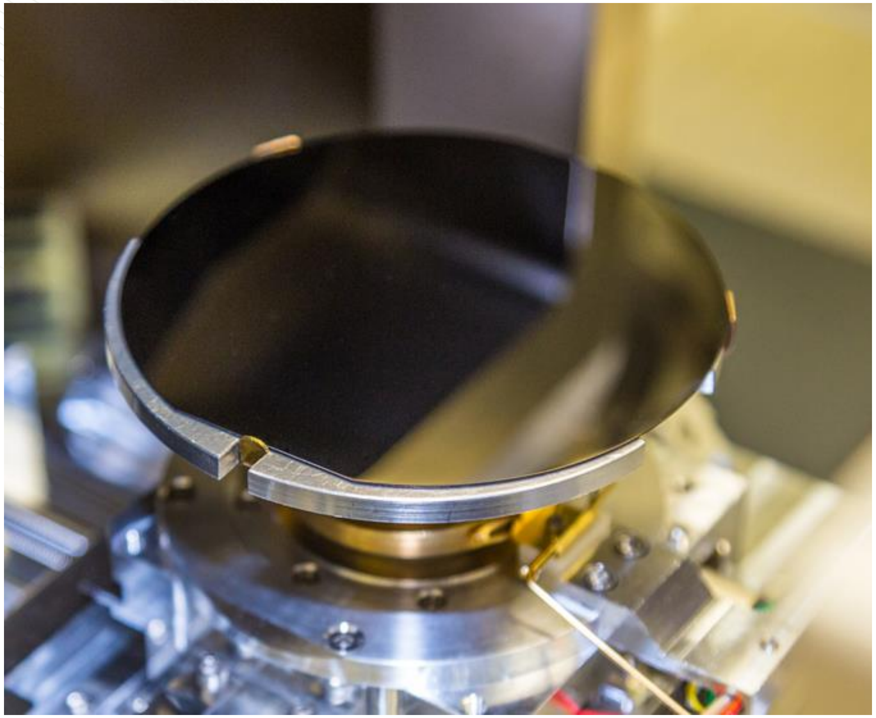




Why?



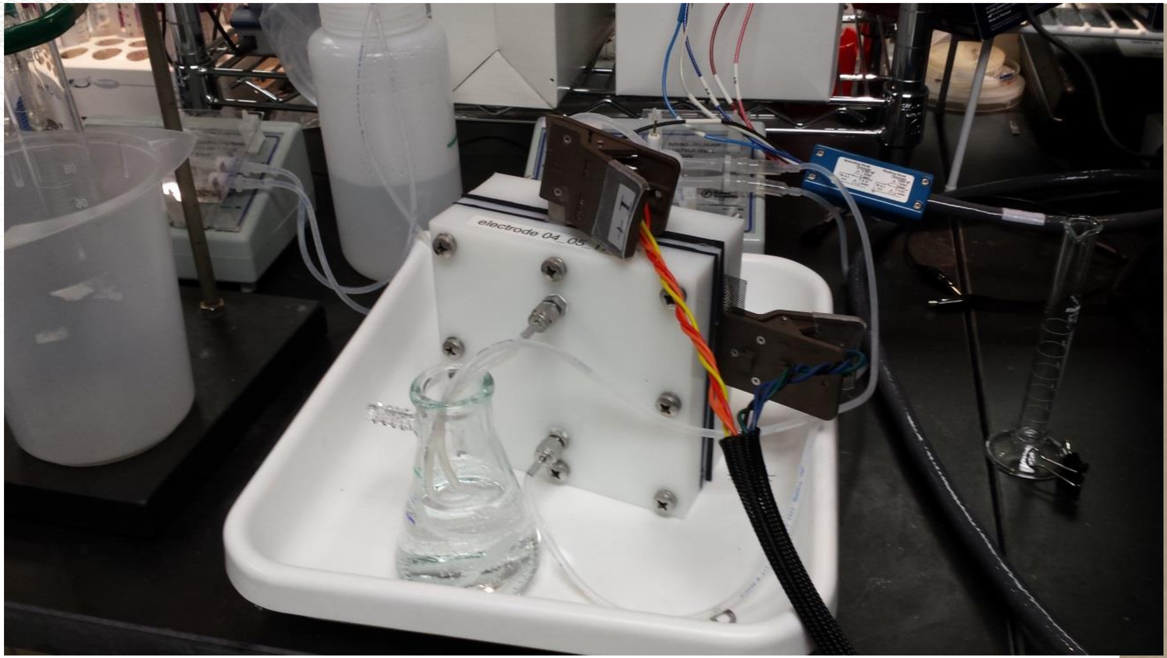
Maturation work: adapted chemical vapor deposition to metallic substrates



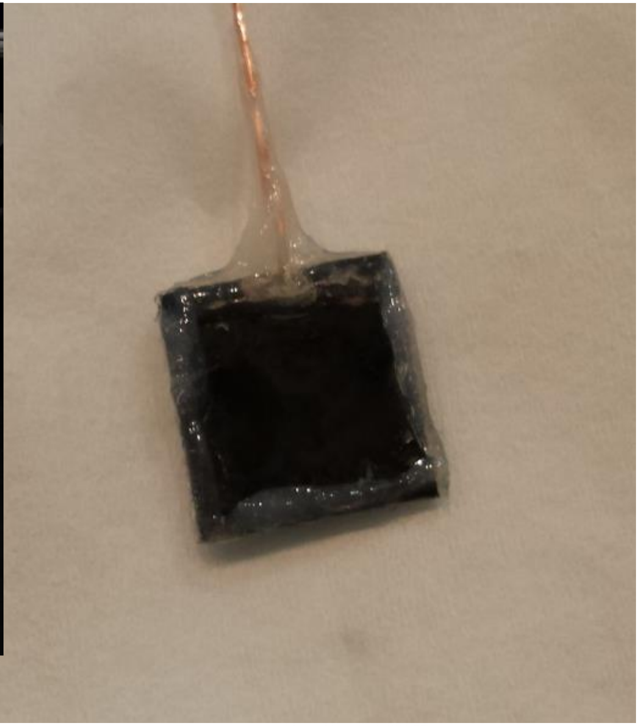
Original nanospikes grown on silicon wafers

Successfully growing nanospikes on metallic substrates

Fabricated large-format electrochemistry cells

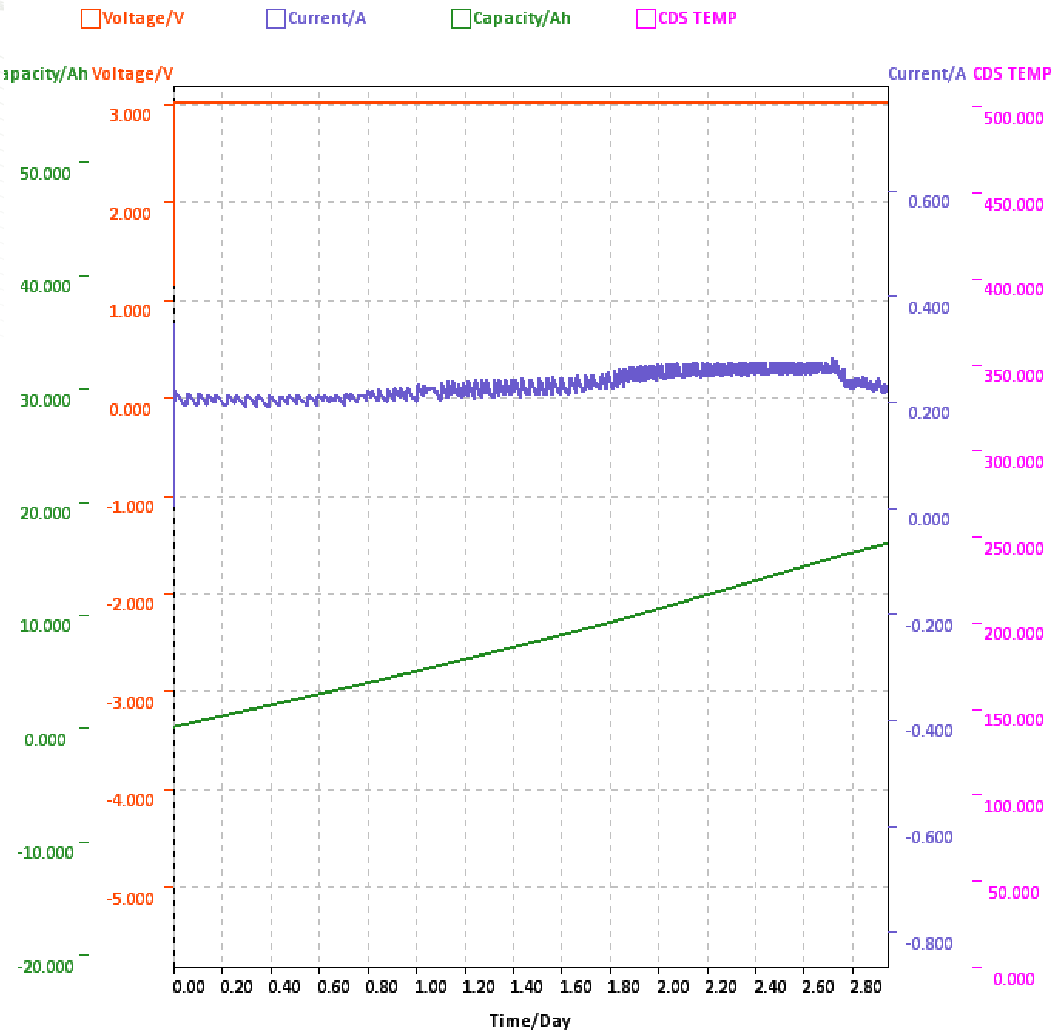


Demonstrator electrode = 100 cm^2



Research electrode =
1 cm^2

Large format cell stability

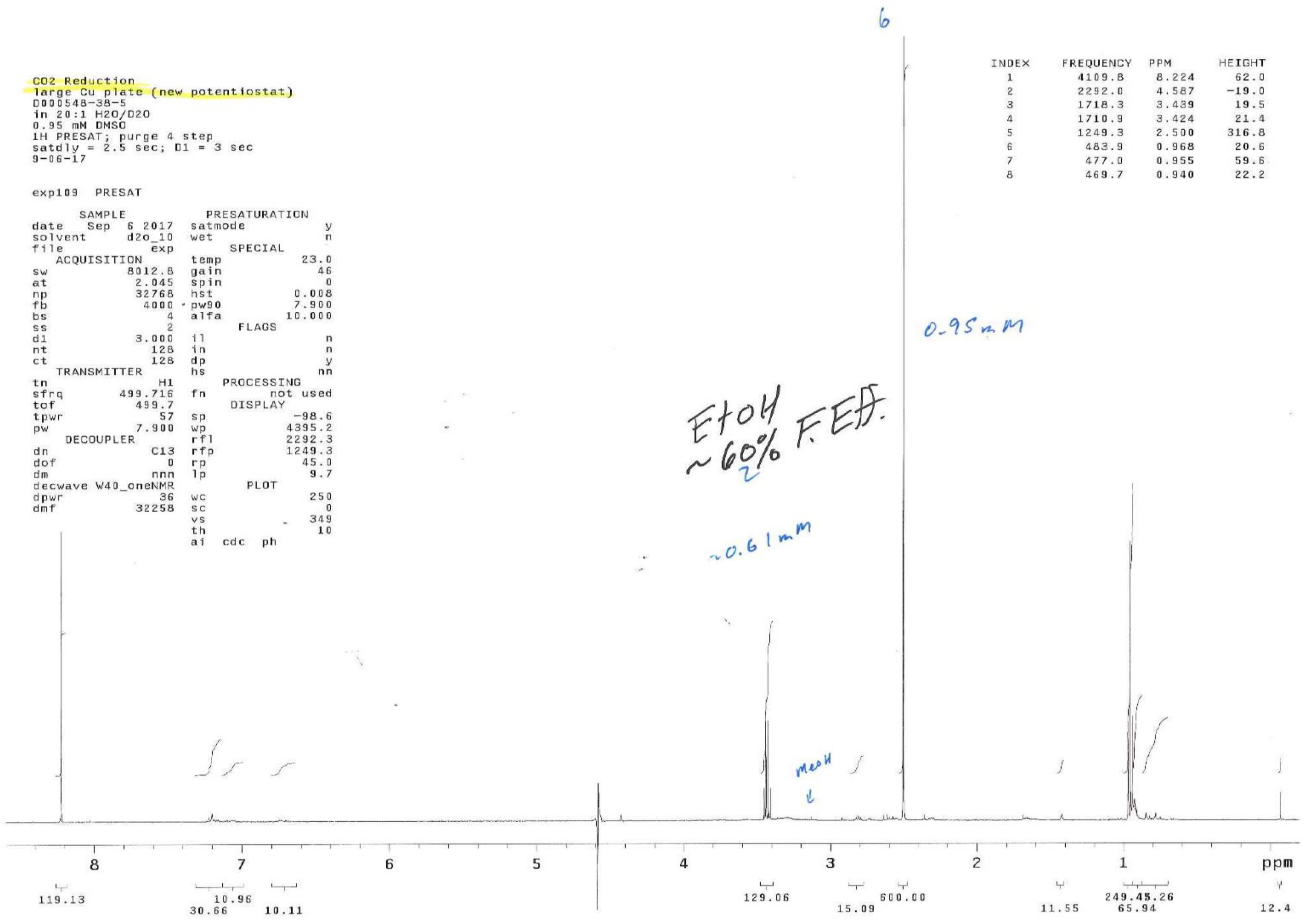


Example: final 3 days of most recent run

Have made significant progress understanding poisoning and lifetime limits

Large Format Results

- Ethanol Produced using a 100 cm^2 electrode
  - (60 nM conc. in 2 h of operation, ~60% F.E.)
- Ethanol Produced using an inexpensive substrate
  - Employing a copper based electrode (100 cm^2)
  - As well as a, perforated S.S. (2 cm^2 electrode)



```
CO2 Reduction
large Cu plate (new potentiostat)
D000548-38-5
in 20:1 H2O/D2O
0.95 mM DMSO
1H PRESAT; purge 4 step
satdly = 2.5 sec; D1 = 3 sec
9-06-17


exp109   PRESAT

      SAMPLE                 PRESATURATION
date    Sep  6 2017   satmode                y
solvent      d2o_10   wet                    n
file            exp           SPECIAL
   ACQUISITION        temp                23.0
sw           8012.8   gain                  46
at            2.045   spin                   0
np            32768   hst                0.008
fb             4000   pw90               7.900
bs                4   alfa              10.000
ss                2           FLAGS
d1            3.000   il                     n
nt              128   in                     n
ct              128   dp                     y
   TRANSMITTER        hs                    nn
tn               H1         PROCESSING
sfrq        499.716   fn              not used
tof           499.7          DISPLAY
tpwr             57   sp                 -98.6
pw            7.900   wp                4395.2
     DECOUPLER        rfl               2292.3
dn              C13   rfp               1249.3
dof               0   rp                  45.0
dm              nnn   lp                   9.7
decwave W40_oneNMR            PLOT
dpwr             36   wc                   250
dmf           32258   sc                     0
                      vs                   349
                      th                    10
                      ai   cdc   ph
```

```
INDEX      FREQUENCY   PPM       HEIGHT
  1          4109.8    8.224       62.0
  2          2292.0    4.587      -19.0
  3          1718.3    3.439       19.5
  4          1710.9    3.424       21.4
  5          1249.3    2.500      316.8
  6           483.9    0.968       20.6
  7           477.0    0.955       59.6
  8           469.7    0.940       22.2
```

6

0.95 mM

EtOH
~60% F.E!

~0.61 mM

MeOH

Rudimentary Economic Estimate

Based on laboratory-scale data
Does not include capital costs

Consider 1g electrochemical ethanol:

$$\left(\frac{1g}{46g/mol}\right) \times 6.02e^{23} \times \frac{12\mathrm{e}^{-}}{molecule} \div \frac{6.24e^{18}\ \mathrm{e}^{-}}{Coulomb} \times 2.99\mathrm{V} = 75.3\mathrm{kJ\ energy\ in}$$

$$\text{Ethanol energy density} = 26.4\ \mathrm{kJ/g}$$

$$\text{Energy Efficiency} = \frac{26.4\mathrm{kJ}}{75.3\mathrm{kJ}} = 35.1\%$$

$$35.1\%\ \times 63\%\ \text{Faradaic Efficiency} = 22\%\ \text{Total Energy Efficiency}$$

H$_2$, CH$_4$ considered throw-away

Consider 1 gallon ethanol:

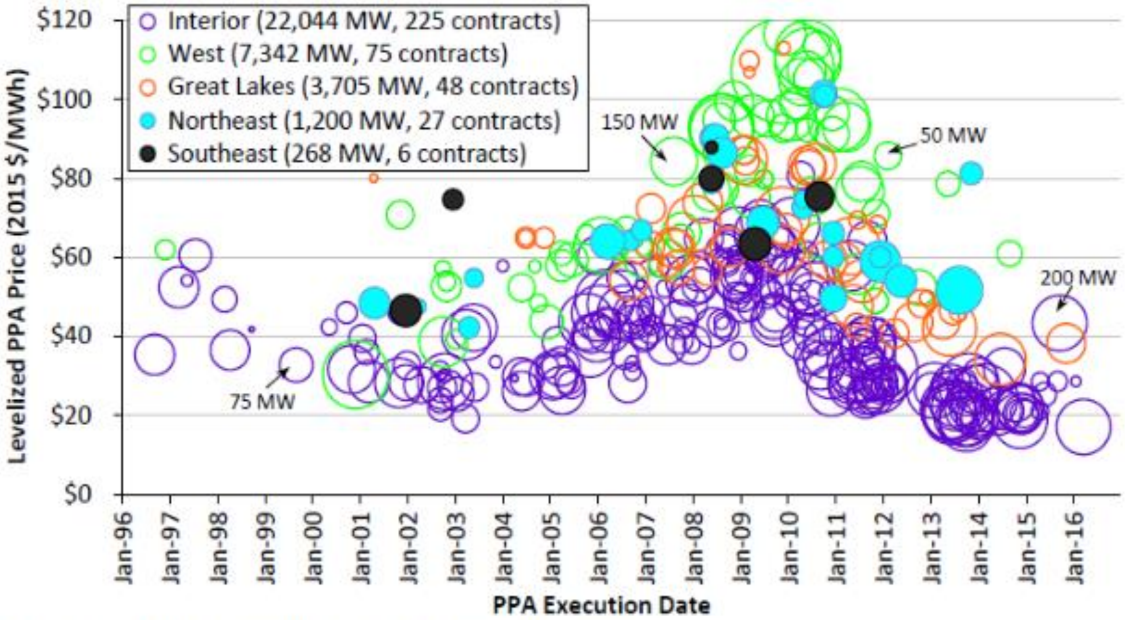
$$78.8\ MJ/gallon = 21.9\ kW \cdot h/gallon$$

$$21.9\ kW \cdot h/gallon\ \div 22\% = 99.2\ kW \cdot h$$

$99.2\ kW \cdot h\ \times \$0.02/kW \cdot h = \$1.98$ per gallon ethanol for electricity

based on laboratory-scale experiments
Not including capital costs

- Commercial overpotential will be lower due to non-Pt counter electrode
- We have observed single-sample efficiencies closer to 25%



Note: Area of "bubble" is proportional to contract nameplate capacity

Source: Berkeley Lab

Figure 47. Levelized wind PPA prices by PPA execution date and region

American Wind Energy Association, 2016

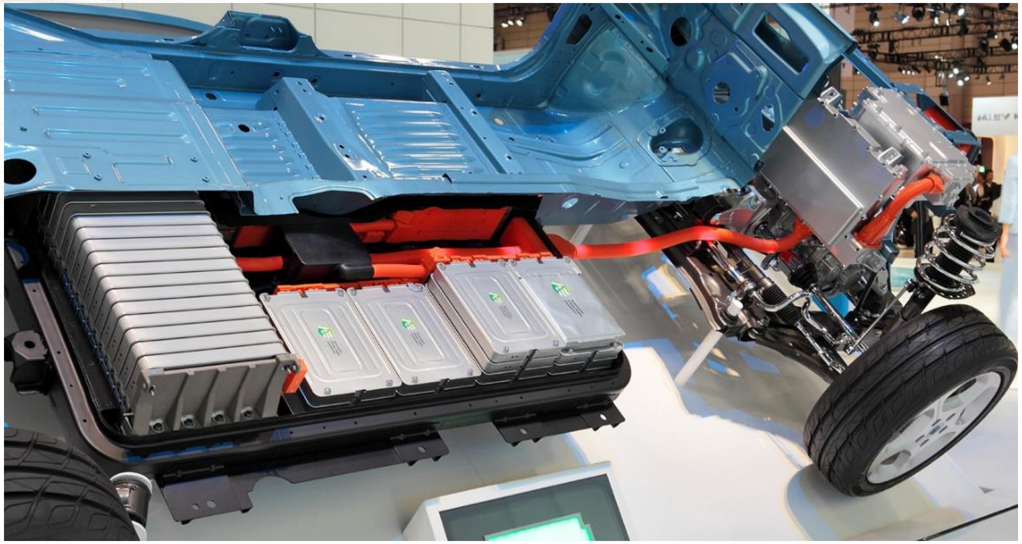
Cost to Drive

	Leaf		Sentra		Sentra EtOH		Sentra EtOH	
Base Cost Car	$30,680.00		$16,990.00		$16,990.00		$16,990.00	
Energy Efficiency Car	2.94	mile/kwh	33	mpg	33	mpg	33	mpg
Lifetime Miles	150000		150000		150000		150000	
Fuel During Lifetime	51020	kwh	4545	gal	4545		4545	gal
Cost Per Unit Energy	$0.09	/kwh residential	$2.00	gal	$3.00	gal	$4.00	gal
Total Cost Fuel	$4,744.90		$9,090.91		$13,636.36	gal	$18,181.82	
Total Cost Lifetime	$35,424.90		$26,080.91		$30,626.36		$35,171.82	
	Does not include charger installation or tax credits							
	Does not include oil, filters, IC maintenance							

Leaf

Sentra

Remove the Capital Cost of the Battery From the Car to the Factory



Portable = small, light, high power density, shape requirements = expensive

Stationary = large, flexible format, serviceable = cheap(er)

Nissan

Thyssenkrupp

Acknowledgement

Dr. Yang Song
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Dr. Zili Wu
Dr. Rui Peng (VA Tech)
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Mr. Dale Hensley

Dr. Bobby Sumpter
Dr. Liangbo Liang
Dr. Harry M. Meyer III
Dr. Miaofang Chi
Dr. Cheng Ma

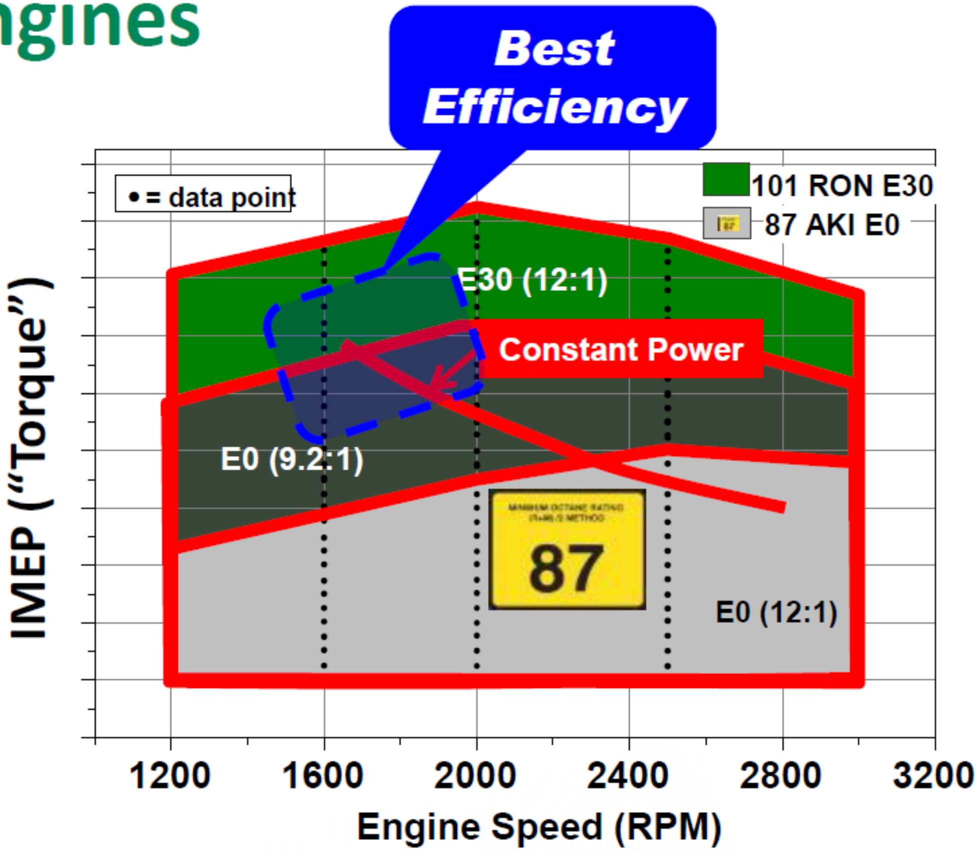
OAK RIDGE
National Laboratory

U.S. DEPARTMENT OF
ENERGY
Office of Science

Chattanooga

Recent Experiments Highlight Efficiency Benefits of High Octane Fuel for SI engines

- Engines can make more torque and power with higher octane fuel
- Ethanol is very effective at boosting octane number
  - 87 pump octane E0 + 30% Ethanol = 101 RON Fuel
- Increased torque enables downspeeding and downsizing for improved fuel economy
- For future vehicles, engine and system efficiency can balance lower energy density of ethanol blends
- ***Every gallon of ethanol could displace a full gallon of gasoline***



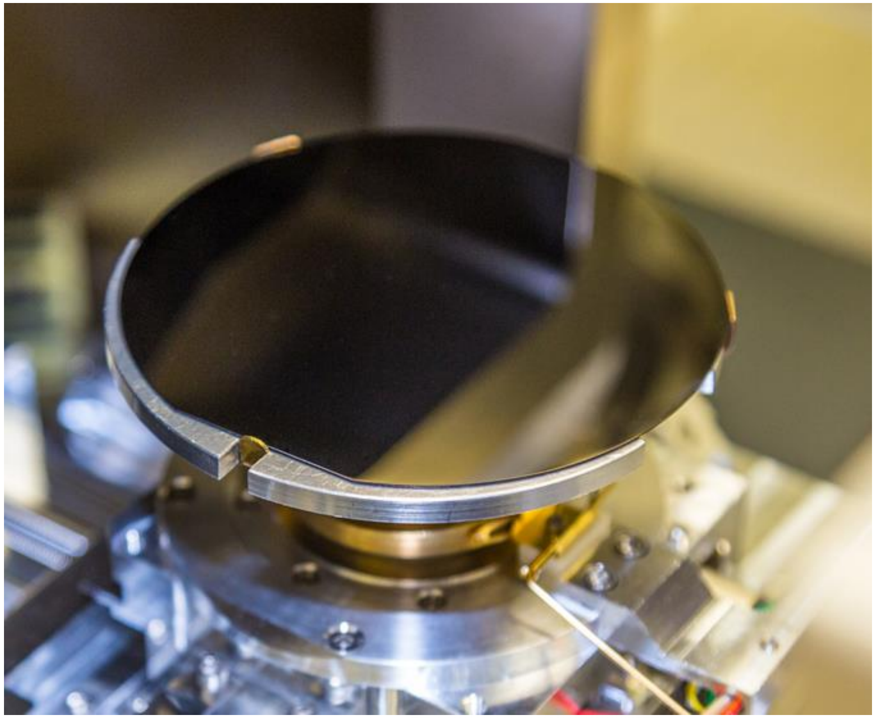
In a high compression research engine, high-octane E30 enables doubling of available torque compared to 87 AKI E0 fuel

- Splitter and Szybist, ORNL

Brian West, ORNL Vehicle Technologies

CNS are Idealized Nano-Carbon

- N-doped: raises Fermi level 0.2 V
- Sharp tips
- Easy to grow over large areas, unlike nanotubes
- No binders necessary to create a film
- No catalysts needed for growth
- No purification
- Grows well on most metals: stainless, Ti, Cu
- Physical and chemical behavior similar to other nano-carbons, with major advantages in scale and reproducibility



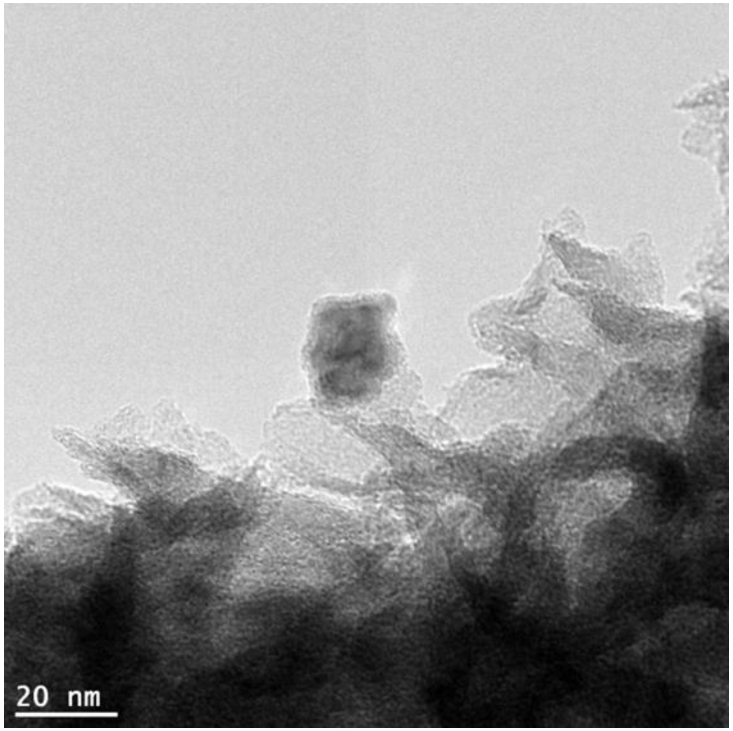
Copper for CO_2 electro-conversion

Previous literature:

- Nanostructured copper on glassy carbon: CH_4
- Textured copper film: CO to ethanol
- Bulk copper plates: mixture of hydrocarbons depending on electrolyte

Y. Hori, K. Kikuchi, A. Murata, S. Suzuki, Chem. Lett. 1986, 15, 897-898.
I. Takahashi, O. Koga, N. Hoshi, Y. Hori, J. Electroanal. Chem. 2002, 533, 135-143.
C. W. Li, J. Ciston, M. W. Kanan, Nature 2014, 508, 504-507.
K. Manthiram, B. J. Beberwyck, A. P. Alivisatos, J. Am. Chem. Soc. 2014, 136, 13319-13325.

- Must minimize H_2 evolution if performed in water

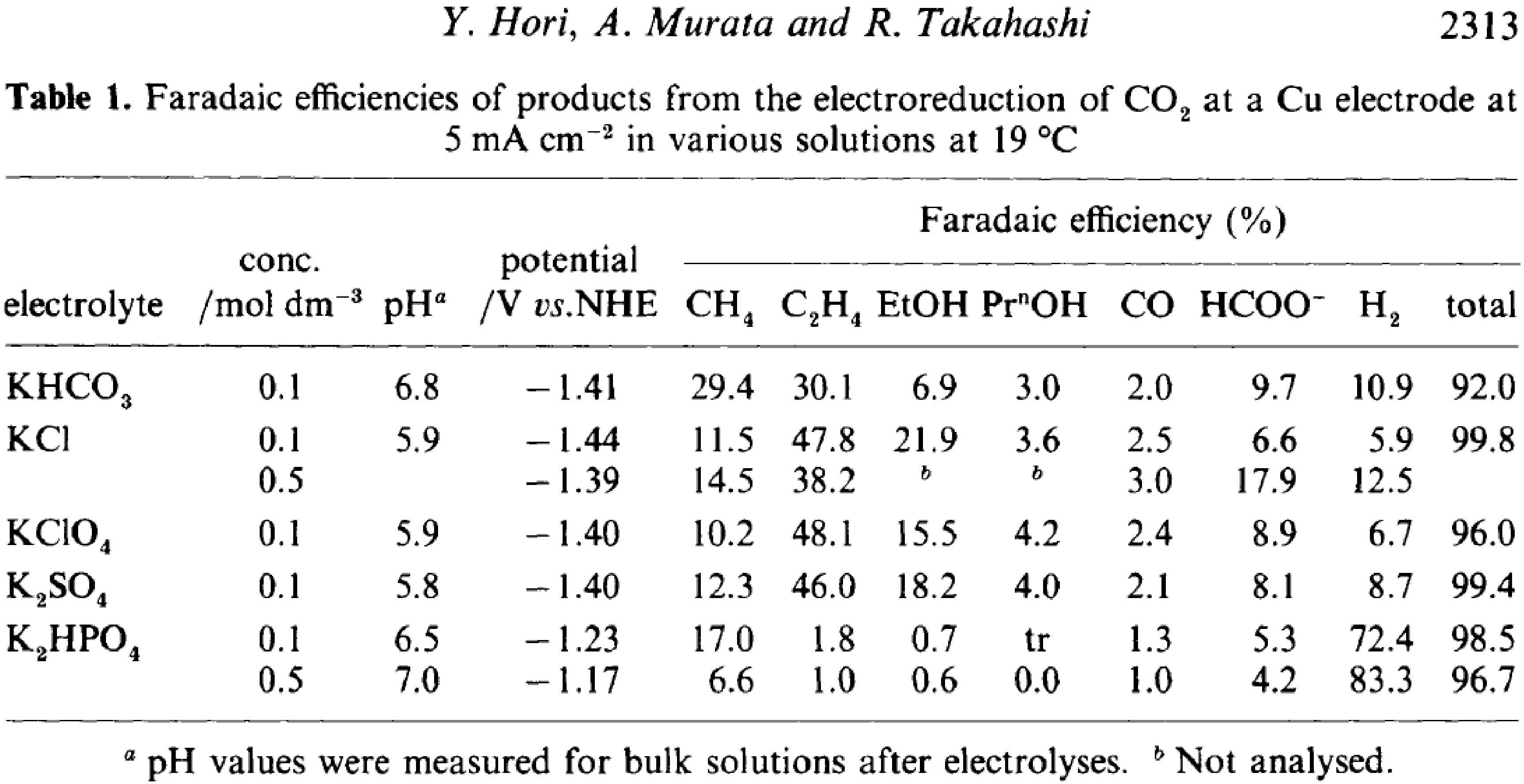


Cu nanoparticle on CNS tip

Cathode reaction for ethanol: $9H_2O + 9e^- \rightarrow 9H + 9OH^-$

$2CO_2 + 9H + 3e^- \rightarrow C_2H_5OH + 3OH^-$

Literature Indicates Diverse Product Mix



Y. Hori, A. Murata and R. Takahashi 2313

Table 1. Faradaic efficiencies of products from the electroreduction of CO_2 at a Cu electrode at 5 mA cm^{-2} in various solutions at 19 °C

electrolyte	conc. /mol dm^{-3}	pH[a]	potential /V *vs.*NHE	Faradaic efficiency (%)							
				CH_4	C_2H_4	EtOH	Pr^nOH	CO	$HCOO^-$	H_2	total
$KHCO_3$	0.1	6.8	−1.41	29.4	30.1	6.9	3.0	2.0	9.7	10.9	92.0
KCl	0.1	5.9	−1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8
	0.5		−1.39	14.5	38.2	[b]	[b]	3.0	17.9	12.5	
$KClO_4$	0.1	5.9	−1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0
K_2SO_4	0.1	5.8	−1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4
K_2HPO_4	0.1	6.5	−1.23	17.0	1.8	0.7	tr	1.3	5.3	72.4	98.5
	0.5	7.0	−1.17	6.6	1.0	0.6	0.0	1.0	4.2	83.3	96.7

[a] pH values were measured for bulk solutions after electrolyses. [b] Not analysed.

J. Chem. Soc., Faraday Trans. 1, 1989, **85**(8), 2309–2326