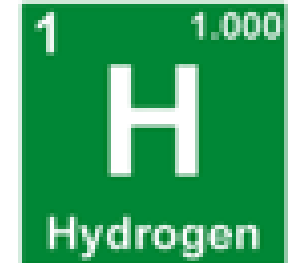
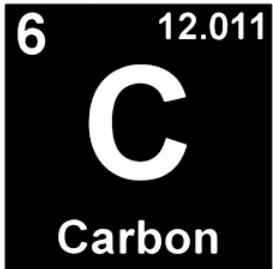


We can use carbon to decarbonize—and get hydrogen for free

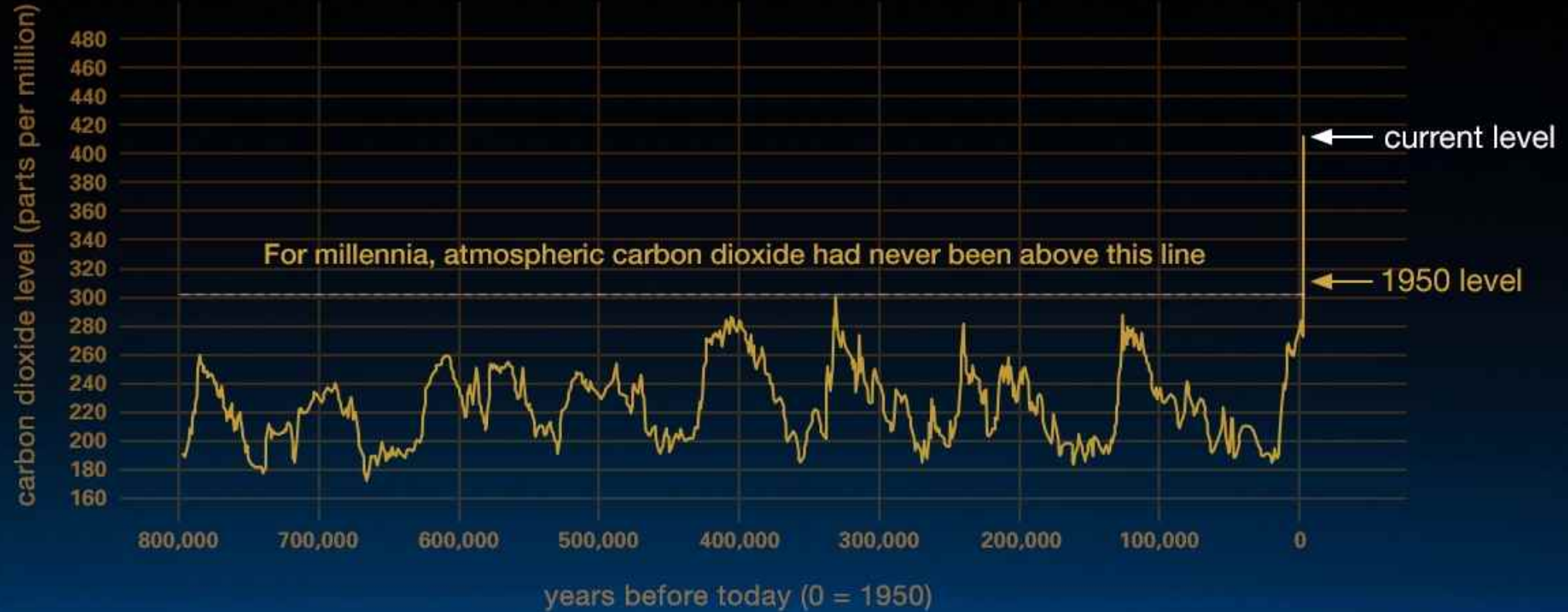


Matteo Pasquali

Departments of Chemical & Biomolecular Engineering,
Chemistry, Materials Science & NanoEngineering
The Carbon Hub; The Smalley-Curl Institute
Rice University, Houston, TX; mp@rice.edu



THE PROBLEM WE ARE FACING



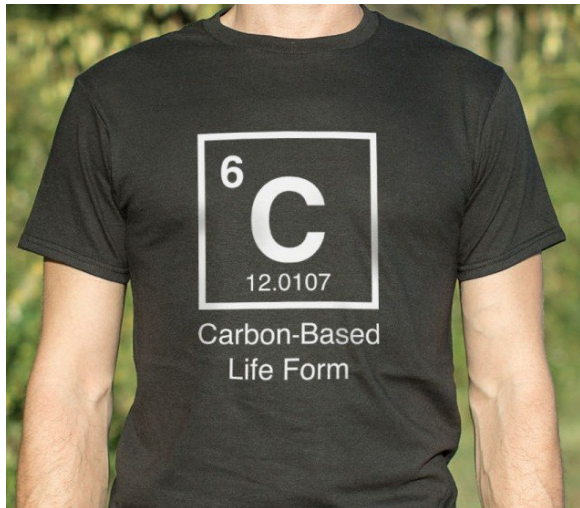
We must decarbonize

THE PROBLEM WE ARE FACING

We are carbon-based life forms

In dry mass

- 50+% of our body is carbon
- 50+% of our food is carbon
- 50+% of our clothes are carbon

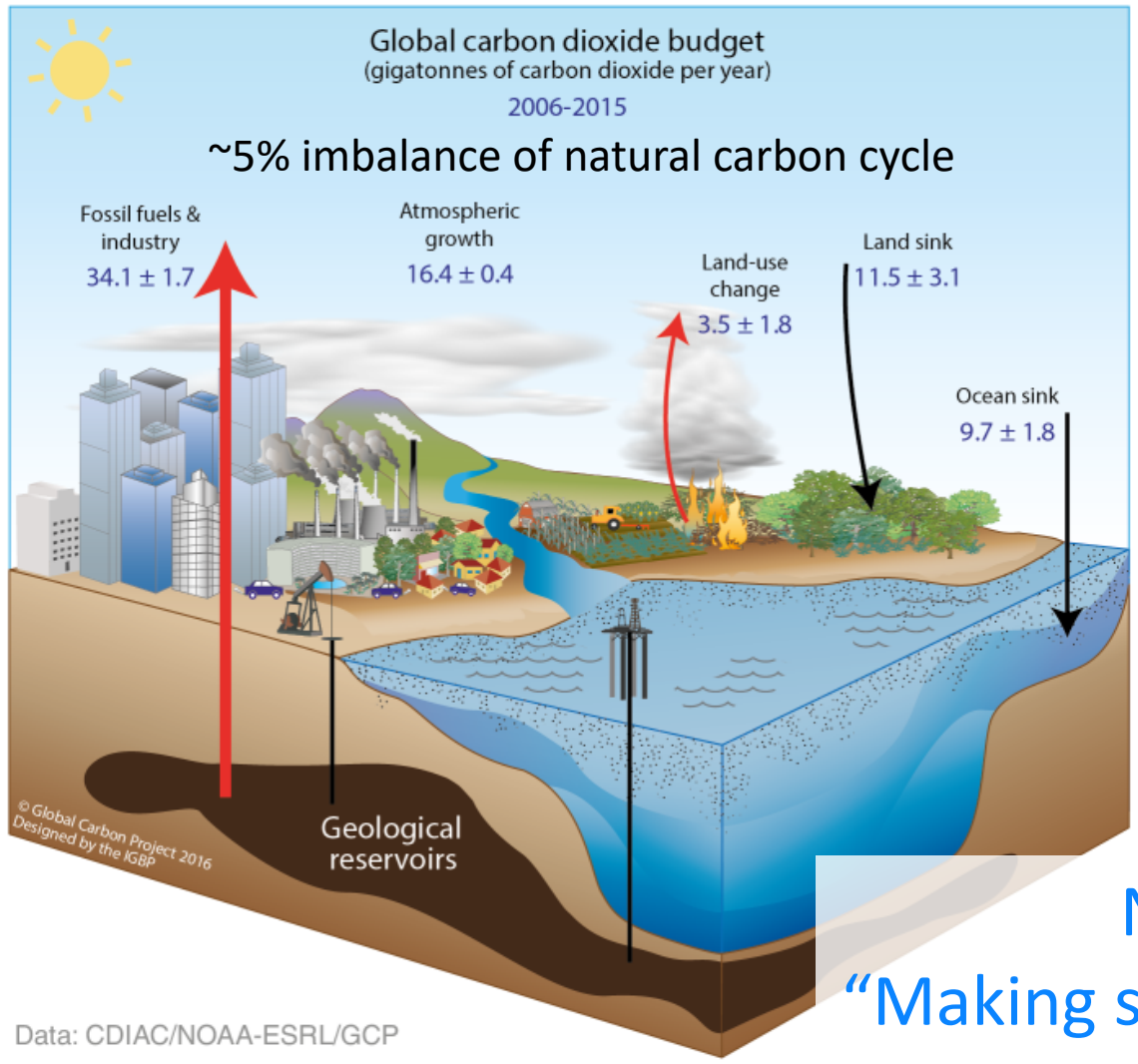


We must **decox**

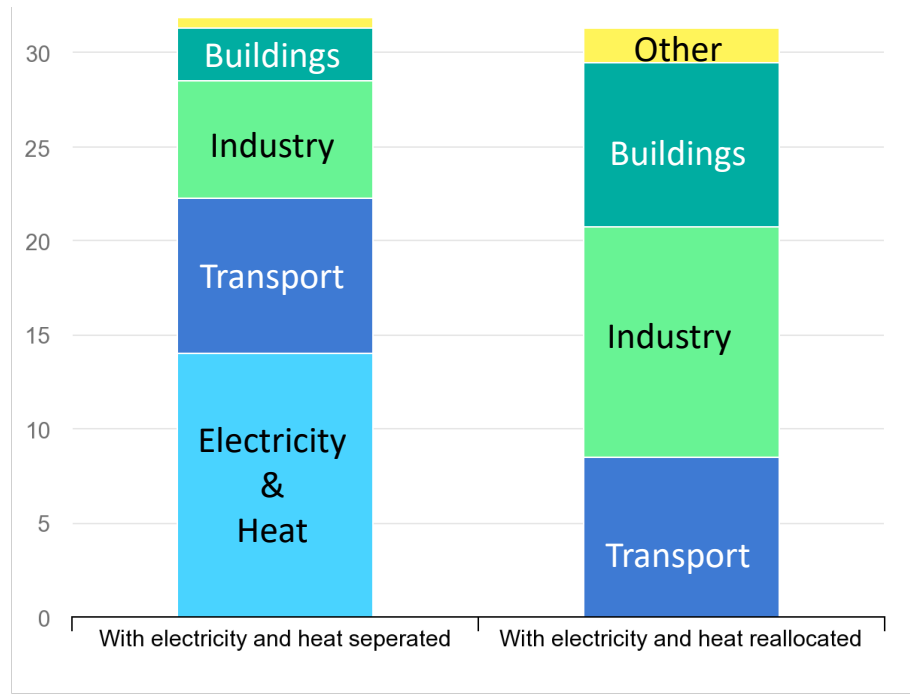
The problem is **C**arbon **Dioxi**d

We have a language challenge: we use the same word for C and **CO₂**

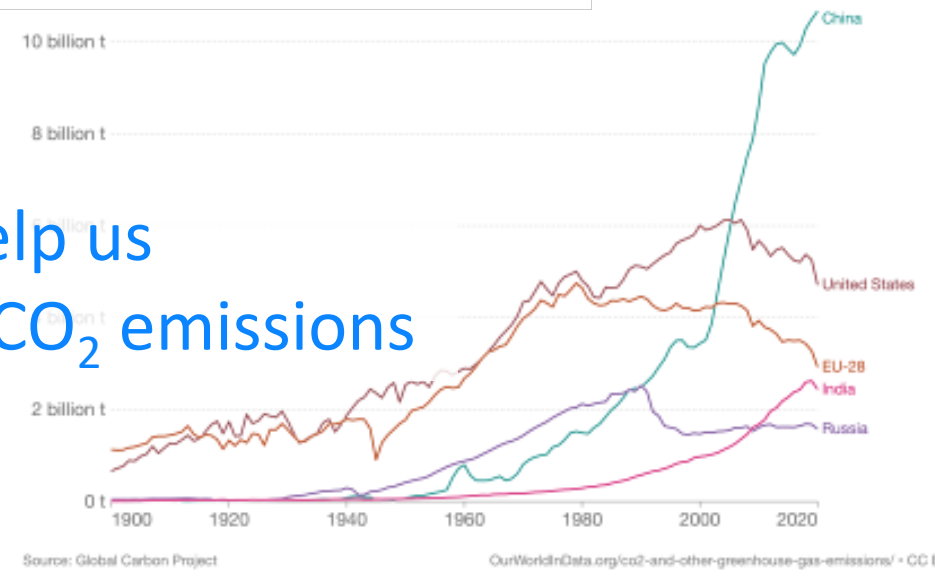
MAN-MADE PERTURBATION OF GLOBAL CARBON CYCLE



Data: CDIAC/NOAA-ESRL/GCP

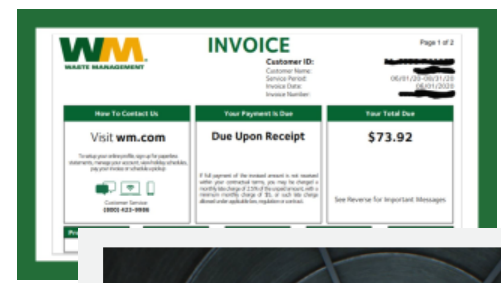


Nature can help us
“Making stuff” causes CO₂ emissions

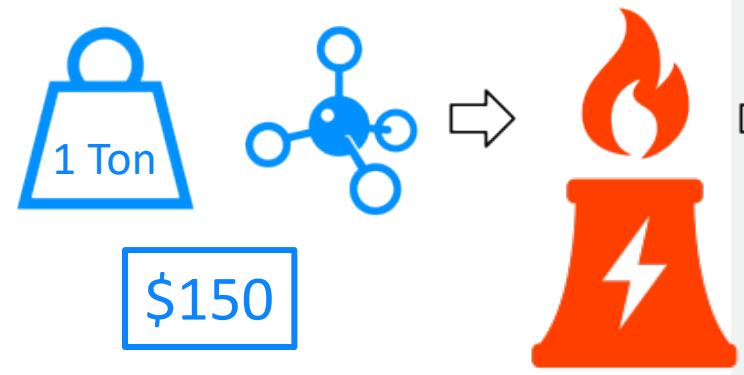


ONE APPROACH: CCS

- Carbon (Dioxide) Capture and Storage
- Sometimes called Carbon Management
- Allows continued use of fossil fuels
- CO₂ as waste management problem
 - Pay to remove
 - Pay to store (landfill)
- Total urban waste: 2 GT/yr
- Total CO₂ emissions: 37 GT/yr
- At 100 \$/Ton for CCS
 - 3.7 Trillion \$/yr business
 - ~60% of the global O&G industry
 - ~5% of world GDP



Can we do better?



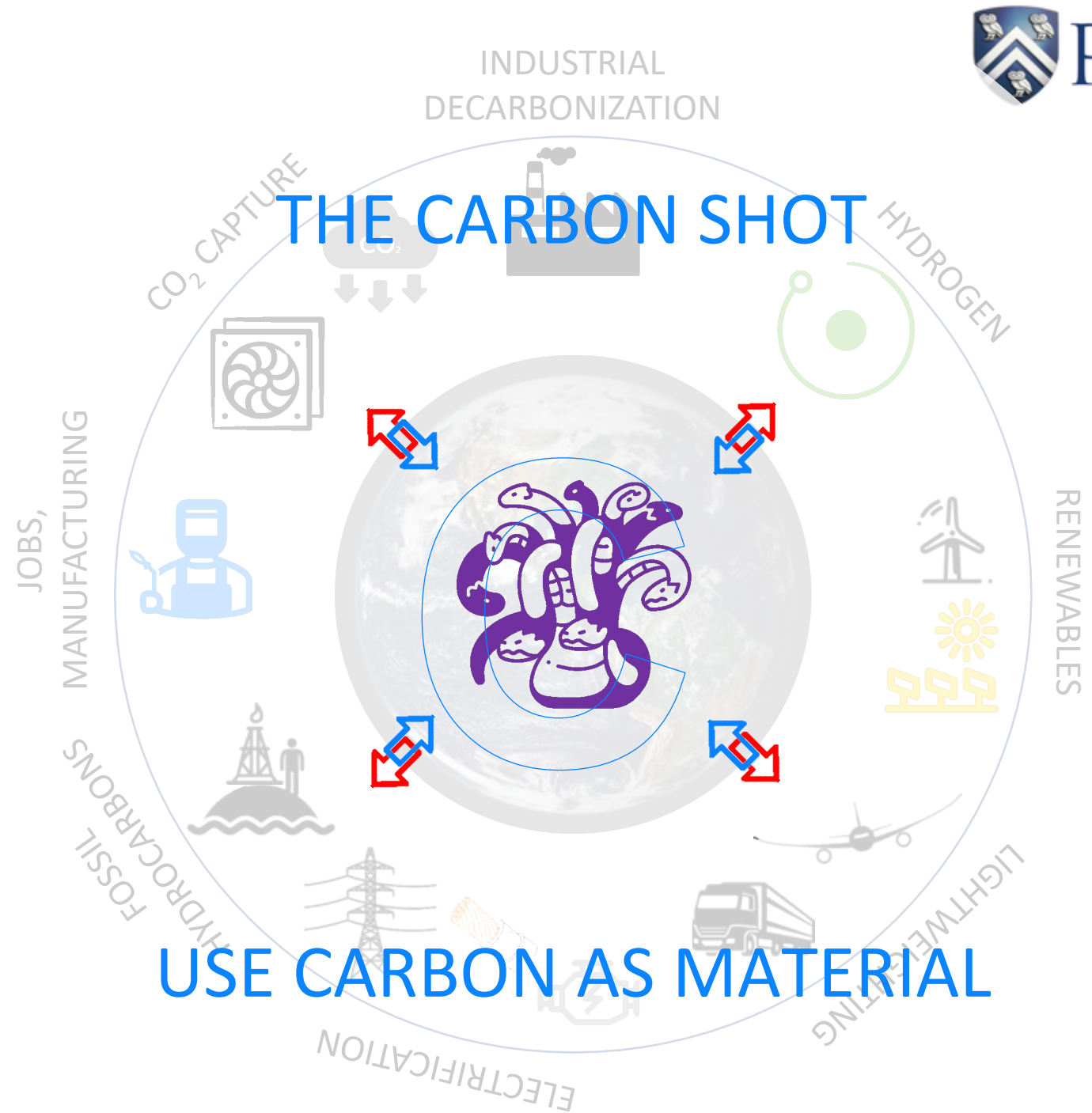
Enhance the CCS Production Tax Credit (45Q) or non-EOR (enhanced oil recovery)

- Initially increase value to ~\$100 per metric ton from current \$50
- Extend eligibility period to 20 years from current 12 years
- Eliminate deadline for starting construction

CLIMATE SOLUTIONS

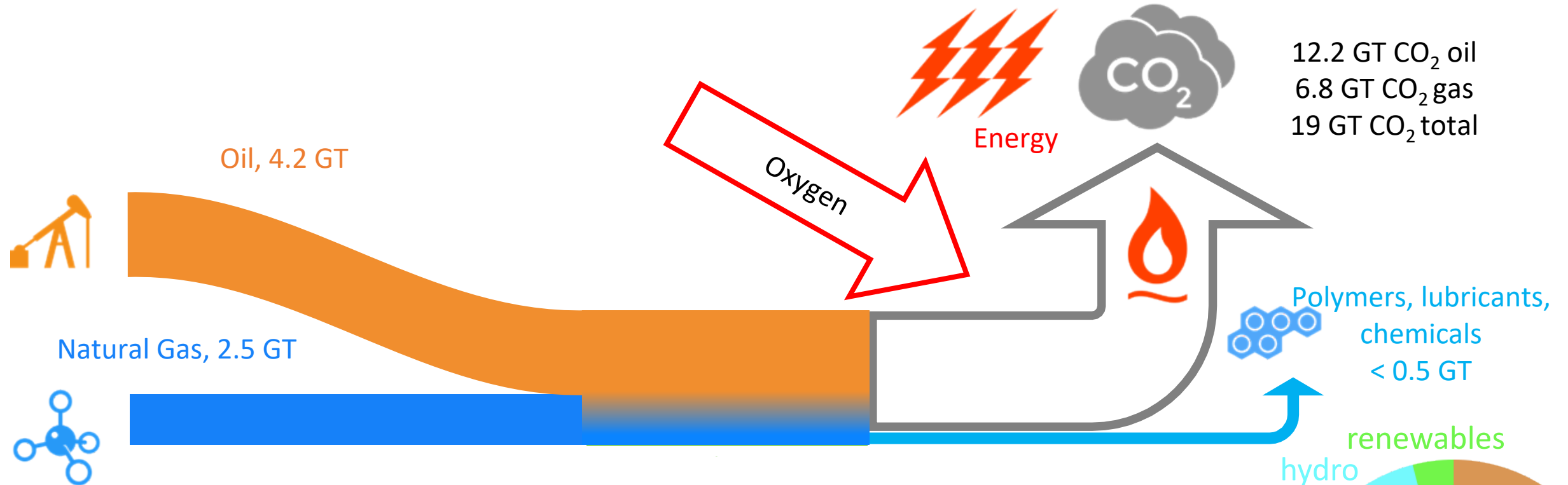
- Multiple climate solutions
 - We need “all of the above”
- Conflicting drivers
 - Each proposed path makes others harder

We’re fighting a Hydra!

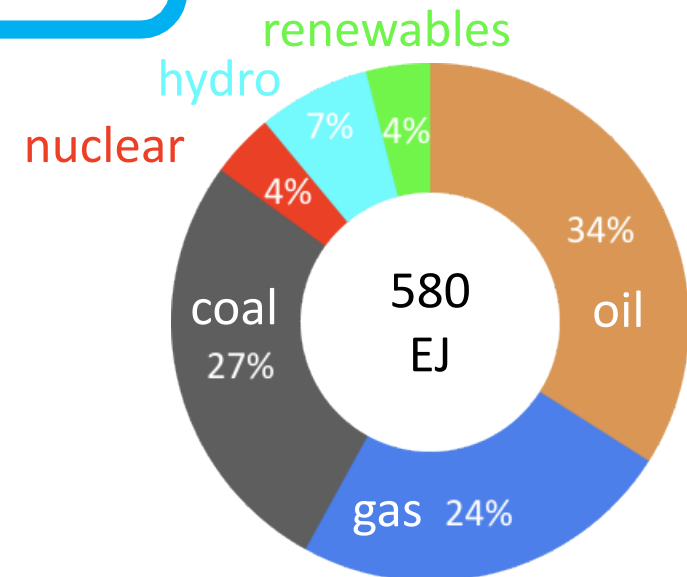


HOW DO WE CURRENTLY USE FOSSIL HYDROCARBONS?

(2017 data)

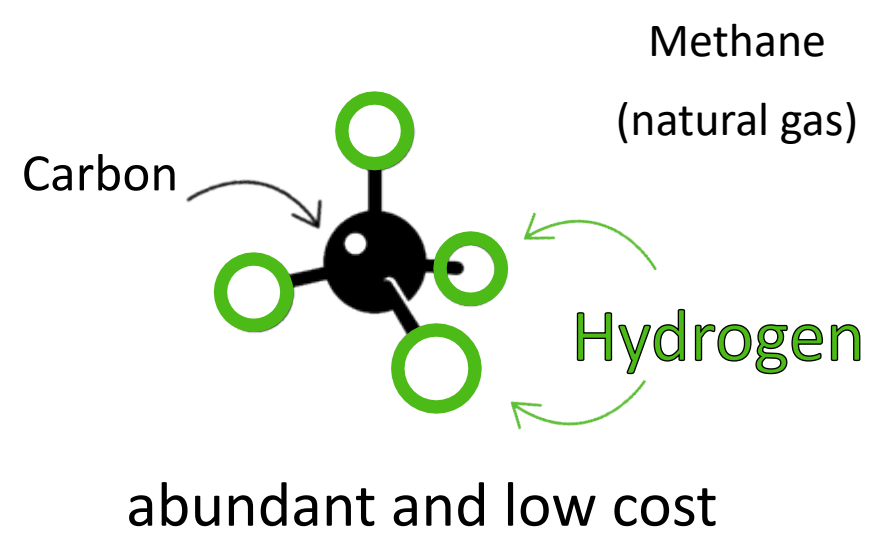


- ⬡ Concurrent pressures:
 - ⬡ Displace fossil fuels with renewables
 - ⬡ Increase energy supply



Can we use the carbon as material?
Can we use the **hydrogen** as energy?

SPLITTING HYDROCARBONS

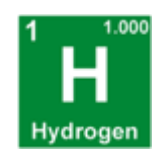


No CO₂ emissions in the splitting process

Efficiency?
Cost?
Policy?

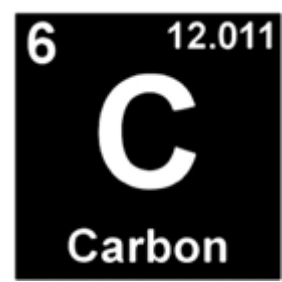
SPLIT

Energy input:
18.8 GJ



1 Ton Hydrogen
(142 GJ energy output)

Commodity



3 Tons
Solid Carbon

Specialty



Current Markets for Carbon Materials

Carbon black	Graphite	Carbon Fibers	Other
15 MT / yr	1 MT / yr	100 kT / yr	50-100 kT / yr

Structural Integrity

Cost

Energy Cost

CO₂ footprint

MAKING STUFF: HOW MUCH MATERIALS DO WE USE?

High value: \$0.8 - 7 / kg
Used in transportation

Big offenders for industrial CO₂ emissions?
Cement, steel, primary metals

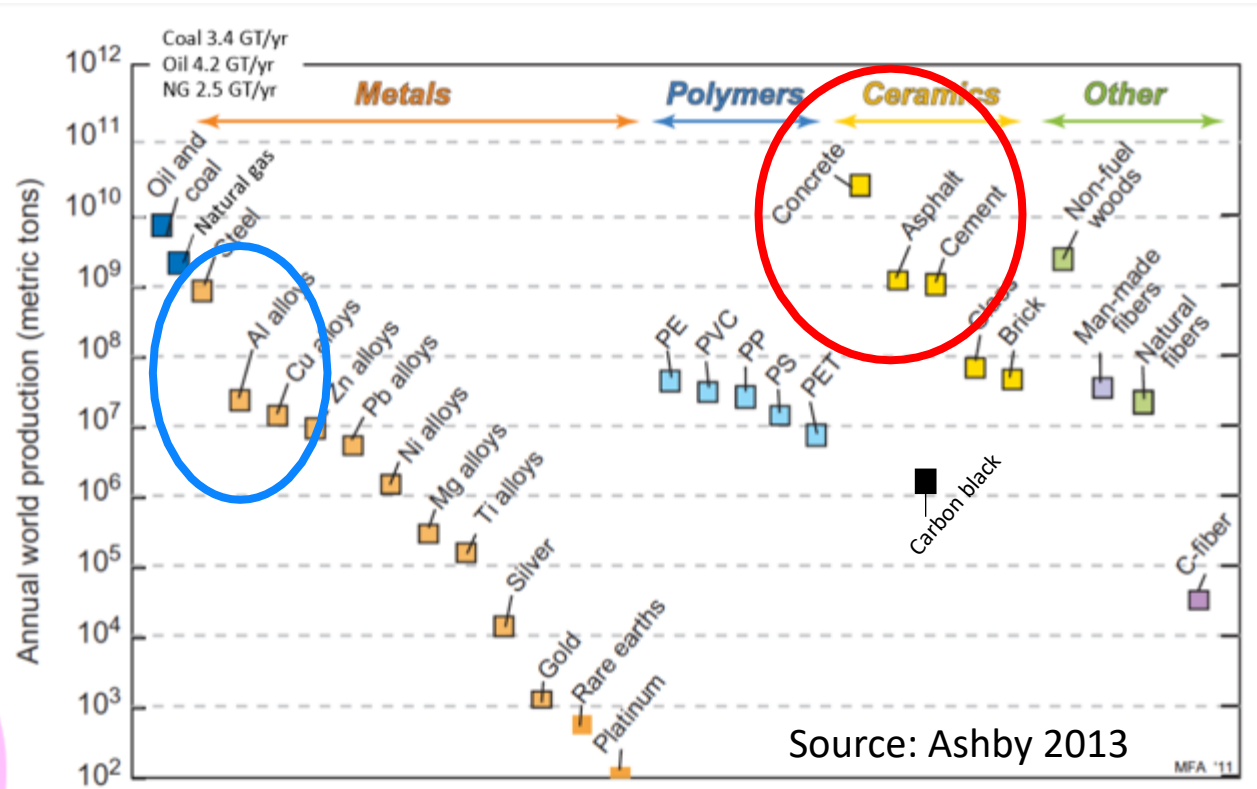
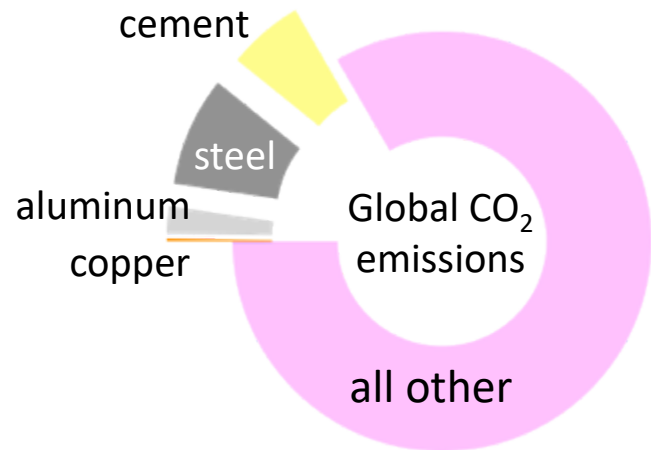


FIGURE 2.3 The annual world production of 27 materials on which industrialized society depends. The scale is logarithmic. The log scale conceals the great differences; the production of steel, for instance, is one billion (10⁹) times larger than that of platinum.

Low value: \$0.05 / kg
Used only in static structures

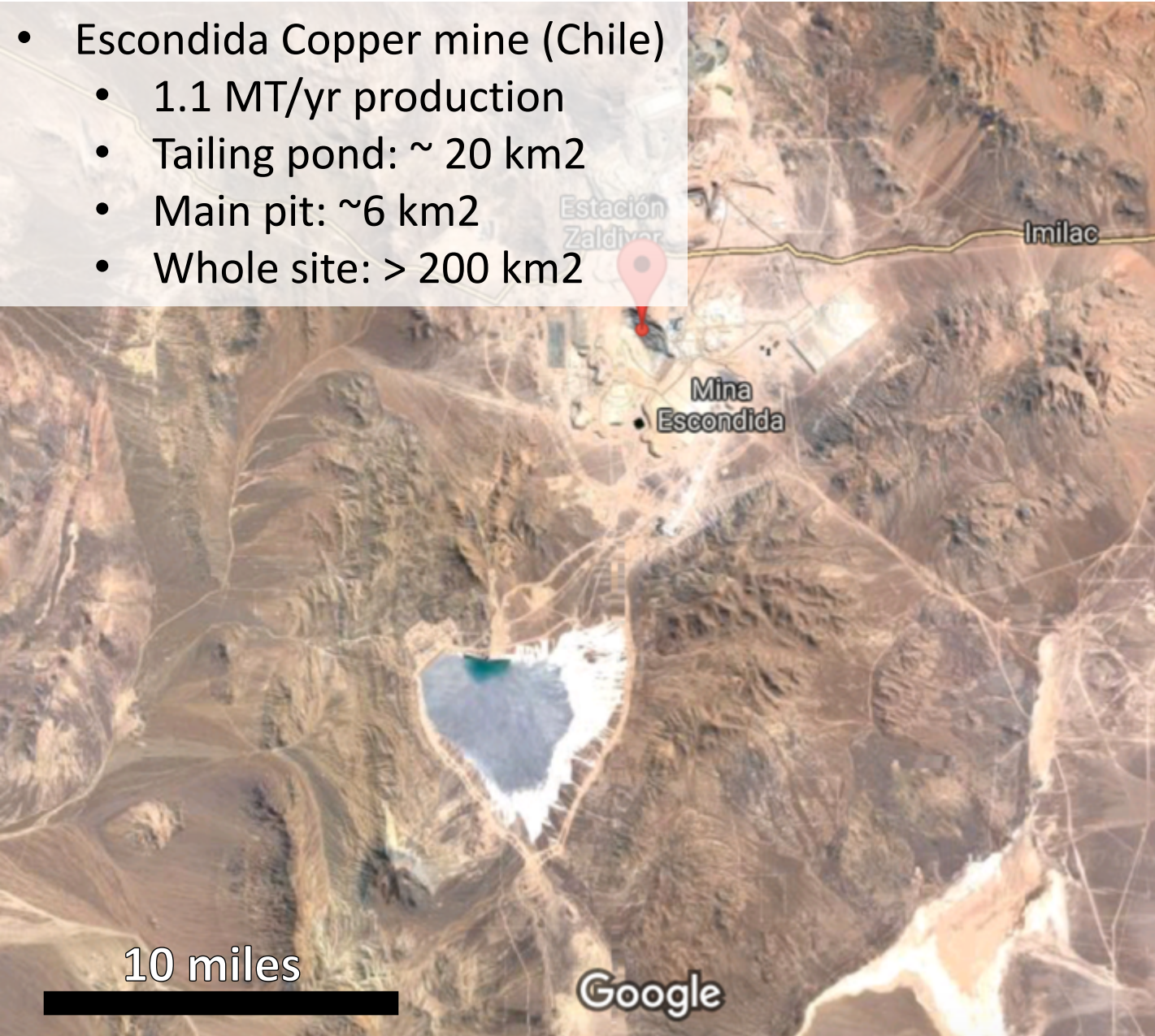


Structural integrity is key for widespread use

The “right” carbon could displace emissions from industrial materials

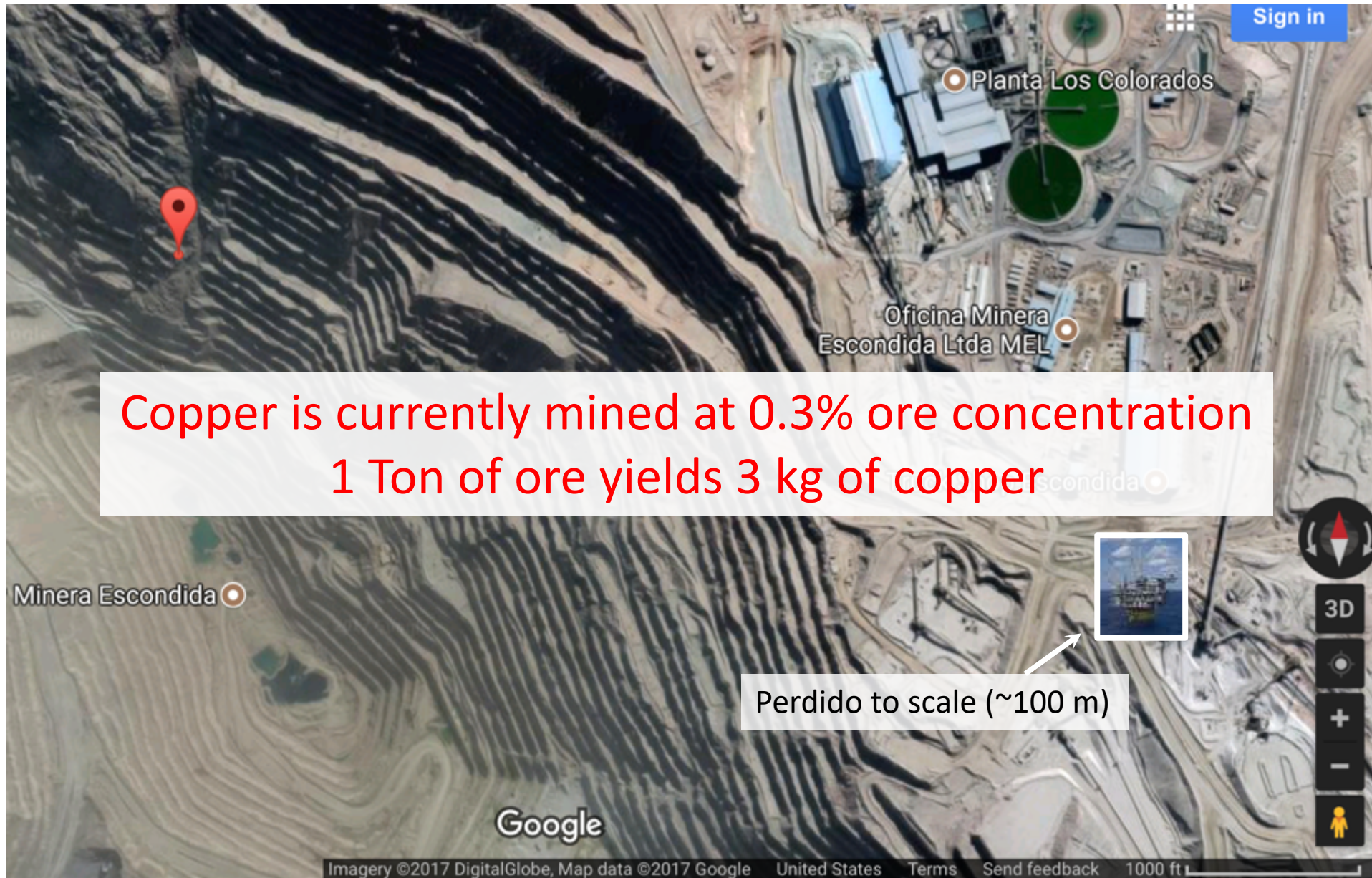
ENVIRONMENTAL IMPACT

- Escondida Copper mine (Chile)
 - 1.1 MT/yr production
 - Tailing pond: ~ 20 km²
 - Main pit: ~6 km²
 - Whole site: > 200 km²



- Perdido oil platform (Gulf of Mexico)
 - Oil: 100 kb/day (5MT/yr)
 - Gas: 200 M cft/day (1.8 MT/yr)
 - 5.5 MT/yr carbon
 - 1 MT/yr hydrogen





INDUSTRIAL SECTOR: MATERIALS-ENERGY-CO₂ NEXUS?



Here's a question you should ask about every climate change plan

-I always ask this question: "What's your plan for steel?"

Bill Gates, August 2019

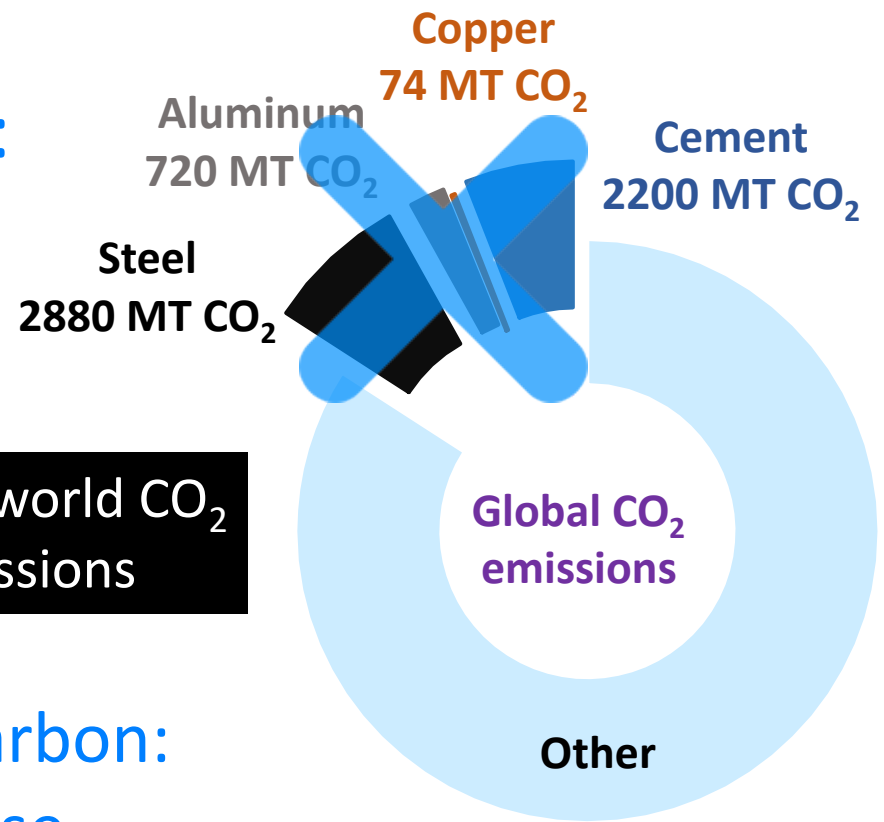
**The plan for steel:
replace it!**

12% of world energy use

16% of world CO₂ emissions

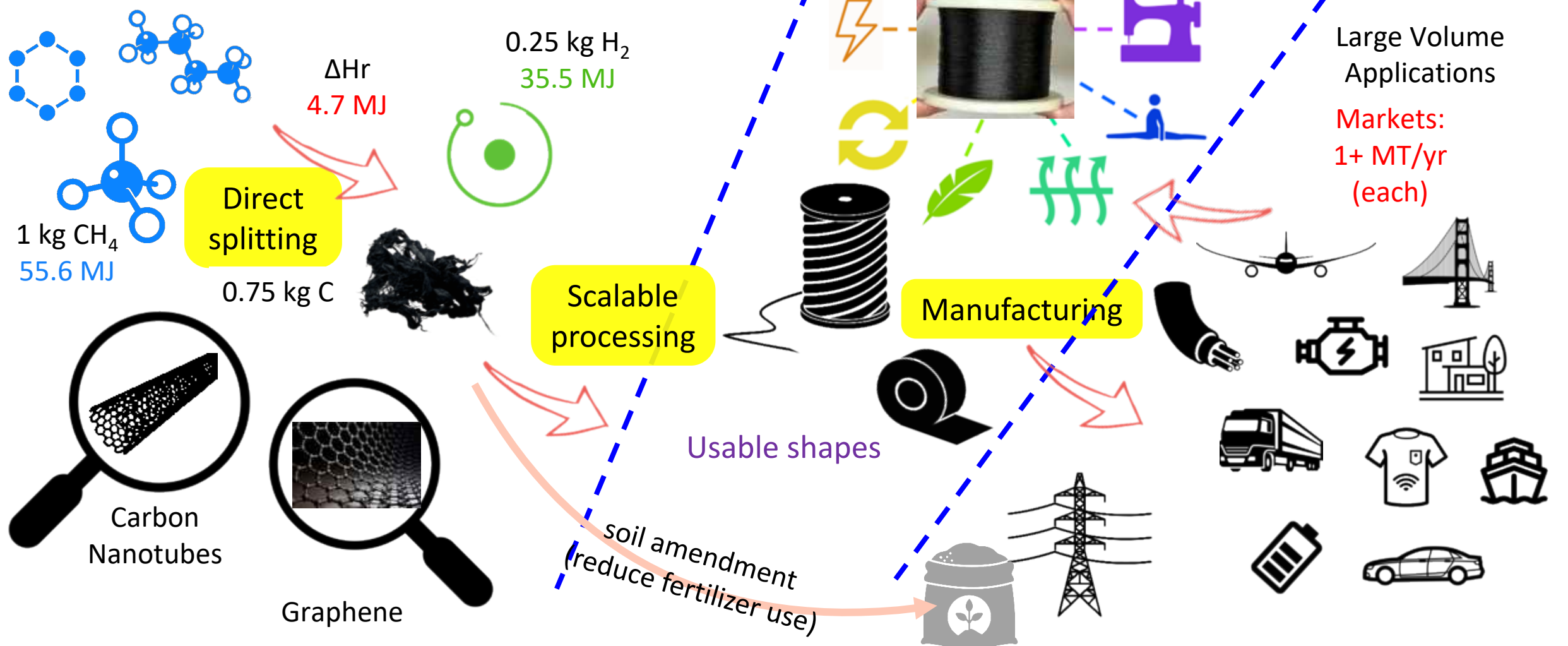
Replacement by carbon:

- Lower energy use
- Eliminate CO₂ emissions



A NEW HYDROCARBON / MATERIAL PATHWAY

- Strip the carbon from the hydrocarbon
- Use the hydrogen for clean energy
- Use the carbon to displace other materials





Dr. Caroline Masiello
 Dr. Dan Cohan
 Dr. Pedro Alvarez
 Rice University



UNSTRUCTURED SOLID CARBON

Amending soil with carbon-rich materials

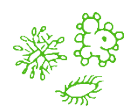
Organic carbon is a key component of soils



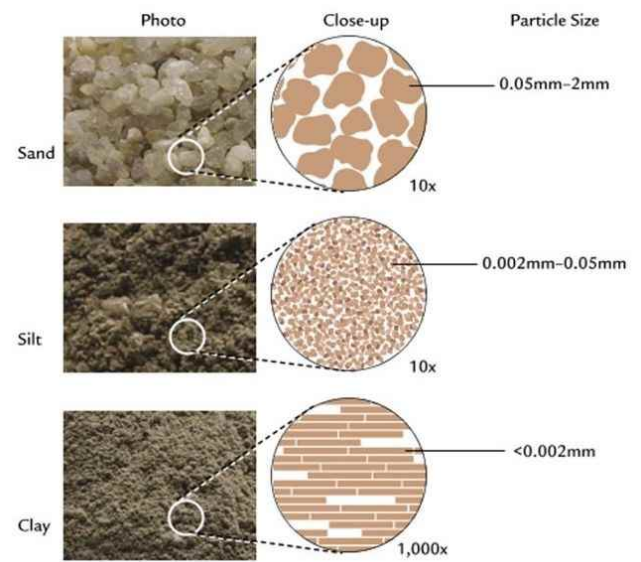
Holds nutrients in plant-available forms:
 less fertilizer pollution / more fertilizer to crops



Improves soil water properties:
 holds more under drought / drains better



Provides microhabitats for microbes that
 support plant growth.



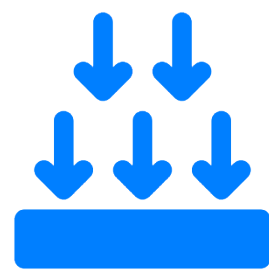
Key properties to improve soils:

- Particle size controls water properties
- Partial charges on organic carbon hold nutrients
- Ability to shuttle electrons

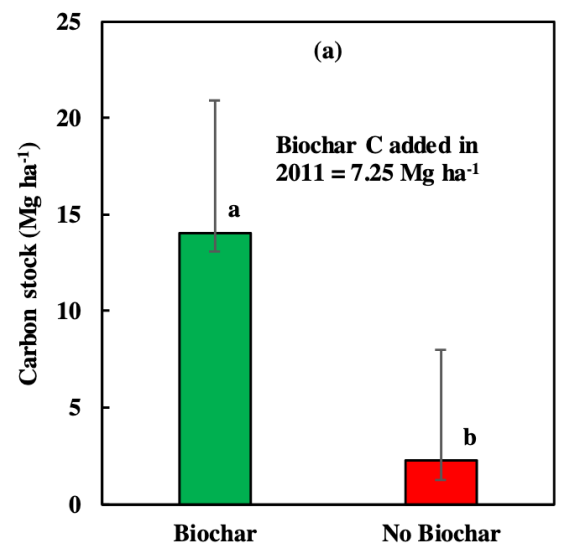
Pyrolytic Carbon potential for soil amendment



Improve soils
 &
 Create a carbon sink



Some forms of carbon such as biochar can be carbon sinks



CARBON BLACK VIA METHANE PYROLYSIS

2021 Focus

monolith

GREEN HYDROGEN PRODUCTION



LAB 1

Laboratory Scale
up to 0.3 kg/hr
2016 – 2018



MINES ParisTech

Pilot Scale
0.3 – 2 kg/hr
2018 – Present



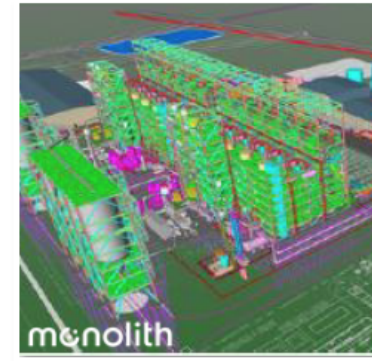
Seaport 1

Demonstration Scale
12 – 18 kg/hr
2014 – 2018



Olive Creek 1

Commercial Scale
540 – 620 kg/hr
2020 – Present



Olive Creek 2

Commercial Scale
6,390 – 7,440 kg/hr
2024

\$1 B loan guarantee from DOE

- Olive Creek 2 will produce 0.18 MT/yr carbon black
- ~1.5% of world carbon market
- 0.06 MT/yr Hydrogen
- Avoid and displace ~1 MT/yr CO₂ emissions

ADVANCED FOSSIL

MONOLITH

HALLAM, NEBRASKA

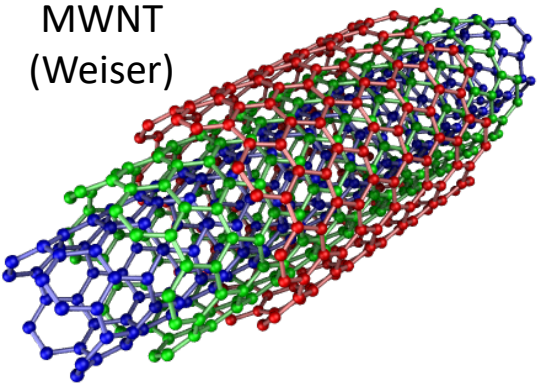
Employing innovative carbon black reactor technology, Monolith is a pioneering clean hydrogen and carbon utilization project.

LOAN GUARANTEE: **CONDITIONAL COMMITMENT**

FINANCED BY U.S. DEPARTMENT OF **ENERGY**

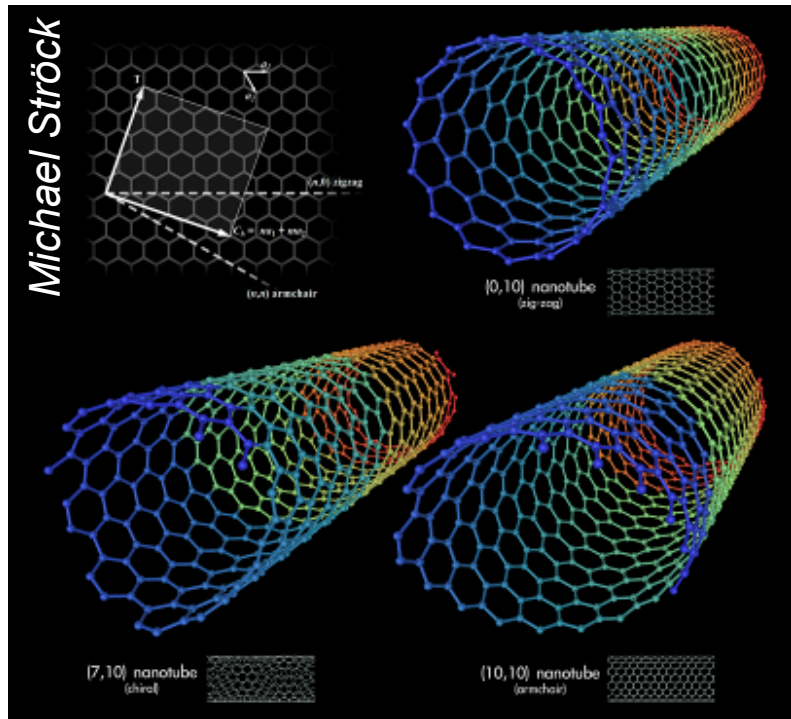
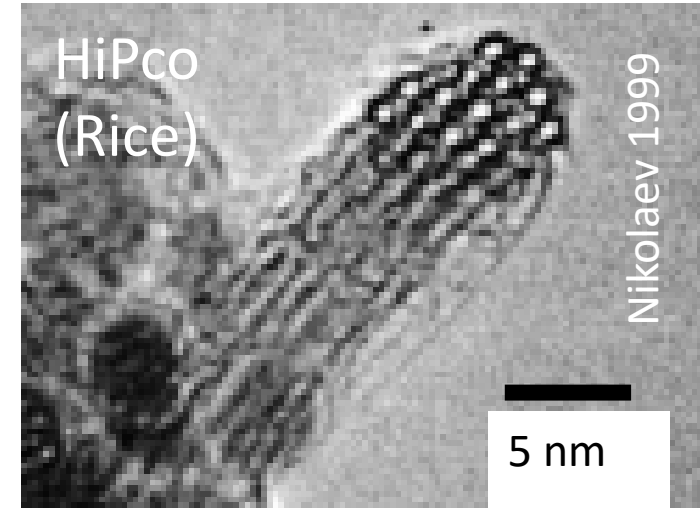
LPO Loan Programs Office

EARLY HISTORY OF CARBON NANOTUBES



EARLY DEVELOPMENTS IN CNT MATERIALS

- ⬡ CNT discovery in 1991 (Iijima)
- ⬡ By mid-1990s, it becomes clear that CNTs are a **material class**
- ⬡ Mid-1990s: focus on CNTs because of applications
- ⬡ Strength ~ 30-40 Gpa (~100x steel)
- ⬡ Elec. Cond ~100 MS/m (~2x Copper)
- ⬡ Thermal Cond ~ 3000 W/ m K (~10x Aluminum)



- ⬡ Large-scale (~10 g) production attained by ~1995 (Smalley)
- ⬡ Very slow application development
 - ⬡ Few application articles by ~2000
- ⬡ Making macroscale materials very difficult
 - ⬡ No control on liquid phases
 - ⬡ No control on macroscopic structures
 - ⬡ No control on macroscopic properties
- ⬡ Late 1990s hype followed by

late 2000s disillusionment



Feasibility Ratings

- 0 = Science Fiction
- 2 = Demonstrated
- 4 = Ready for Market

Scientific American, December 2000

CARBON NANOTUBES NOW

Vibrant Ecosystem of Companies & Labs



COI: MP co-founded DexMat



CNT braided rope



CNT film

Galvorn

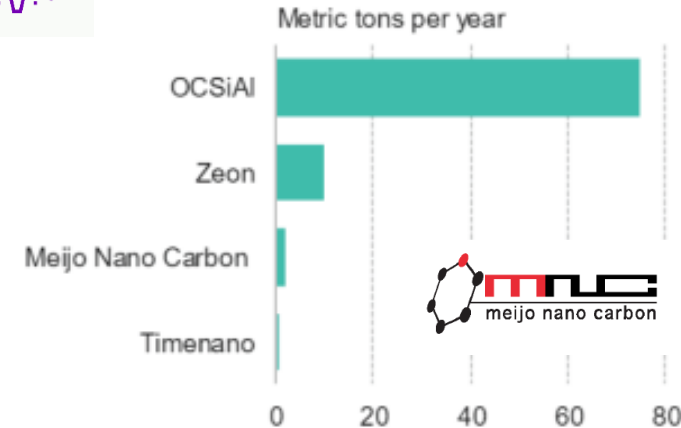


This future is already here!

(just not very evenly distributed...)



World production of carbon nanotubes (fiber-grade)



~120 tons / year in 2021

Source: BloombergNEF, NEDO, Company websites.

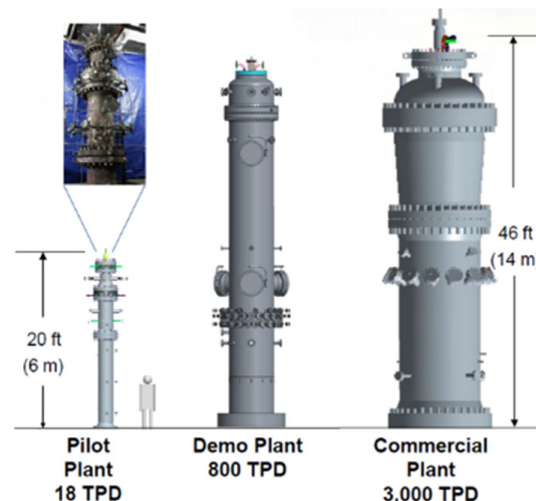


HUNTSMAN

nanocomp TECHNOLOGIES, INC. A Huntsman Company

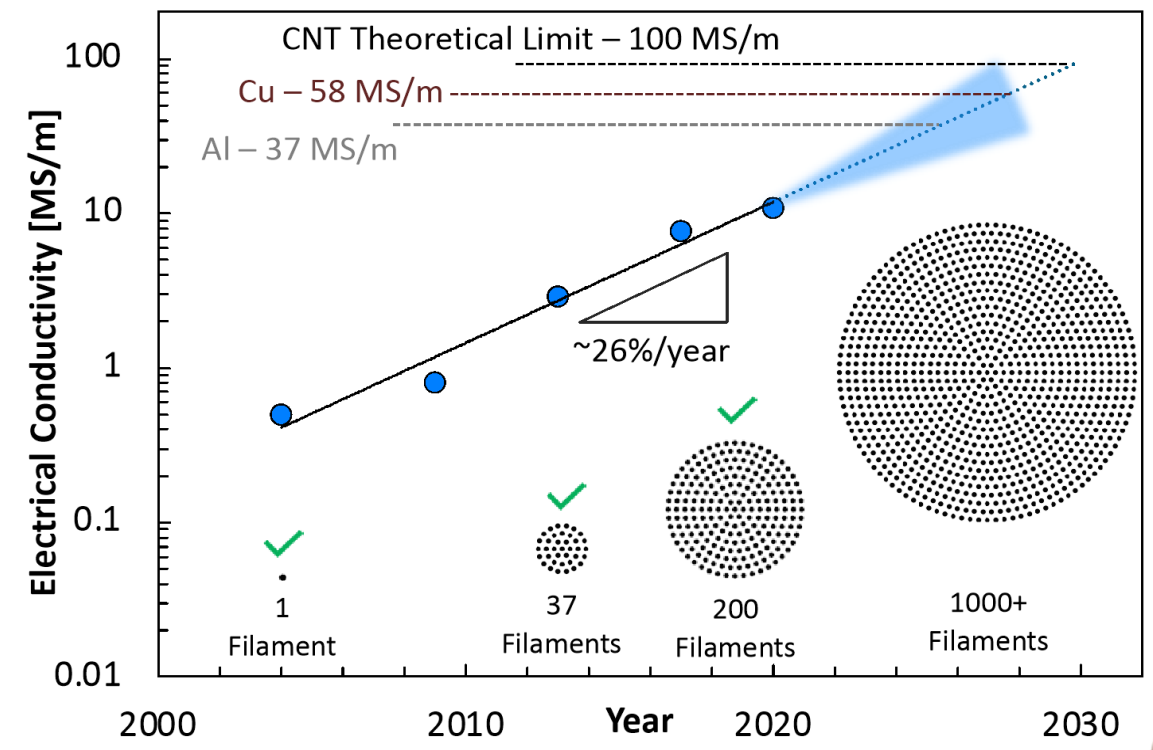
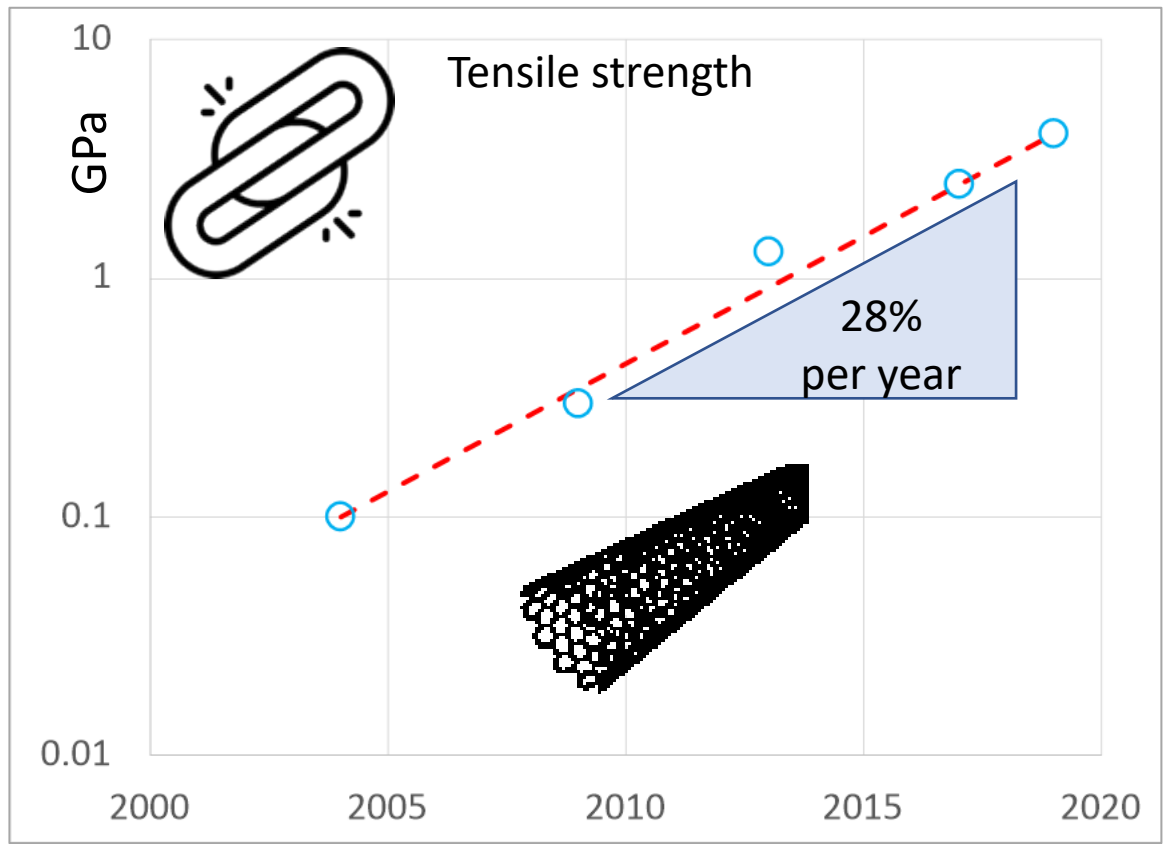


Miralon



No longer a laboratory curiosity

PROPERTIES DEVELOPMENT: LEARNING CURVES

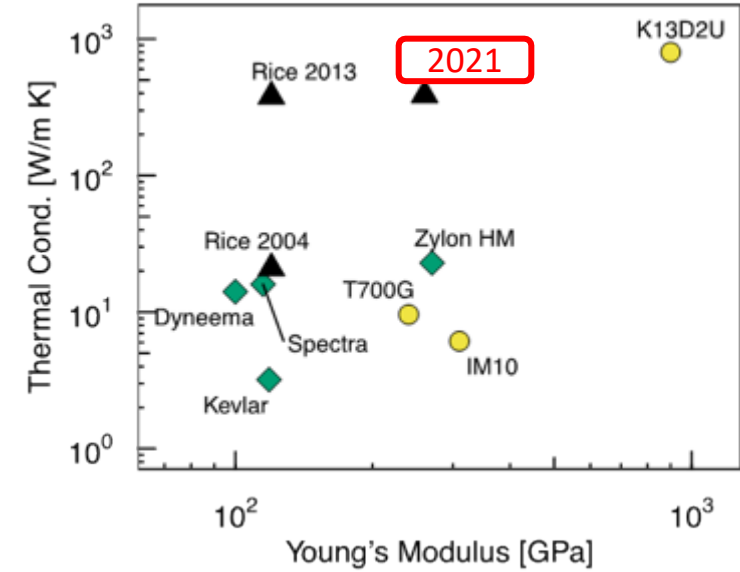
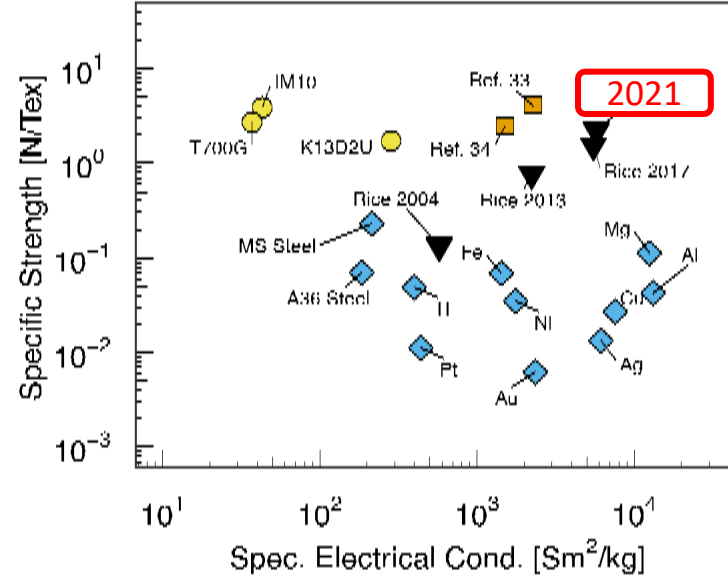
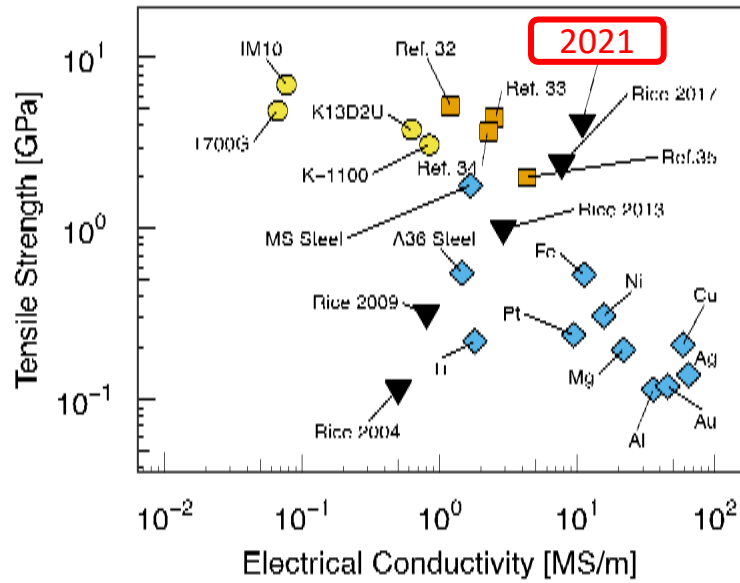


- Very steep property improvement
 - Doubling every 3 years
- Available in **km-length, mm-diameter**
 - wires, tapes, fabrics (Galvorn)
- R&D is continuing



DISPLACEMENT OF METALS & CARBON FIBERS

L. W. Taylor, O. S. Dewey, M. Pasquali, et al., *Carbon*, 2021



- Carbon Fiber
- Direct Spun CNT
- ◆ Metals
- ▲ Polymers
- ▼ Solution Spun CNT

- high strength (~4 GPa) ✓
- high stiffness (~250 GPa) ✓
- high electrical conductivity (~11 MS/m) ✓
- high thermal conductivity (~400 W/ m K) ✓
- low coefficient of thermal expansion ✓
- earth-abundant content ✓
- recyclable and safe for EOL ✓

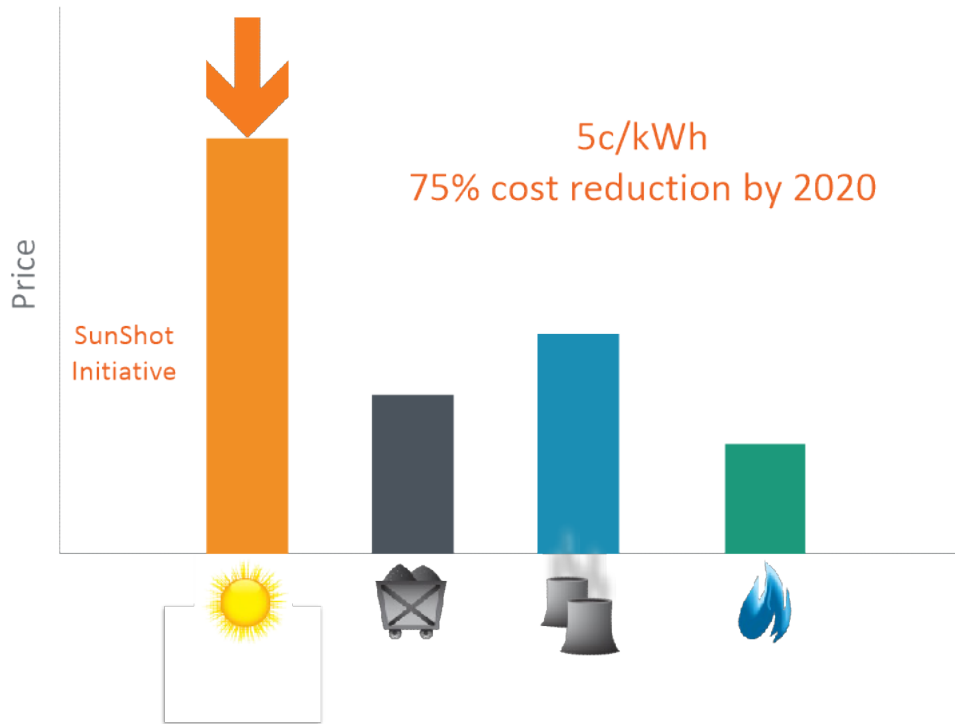
- low density (~ 1800 kg/m³) ✓
- high ampacity ✓
- corrosion-resistant (carbon) ✓
- high bending fatigue strength ✓
- high operating temperature ✓
- high flexibility ✓

WHAT NEEDS TO HAPPEN?

- From solar energy playbook
- Attain cost-parity with incumbents

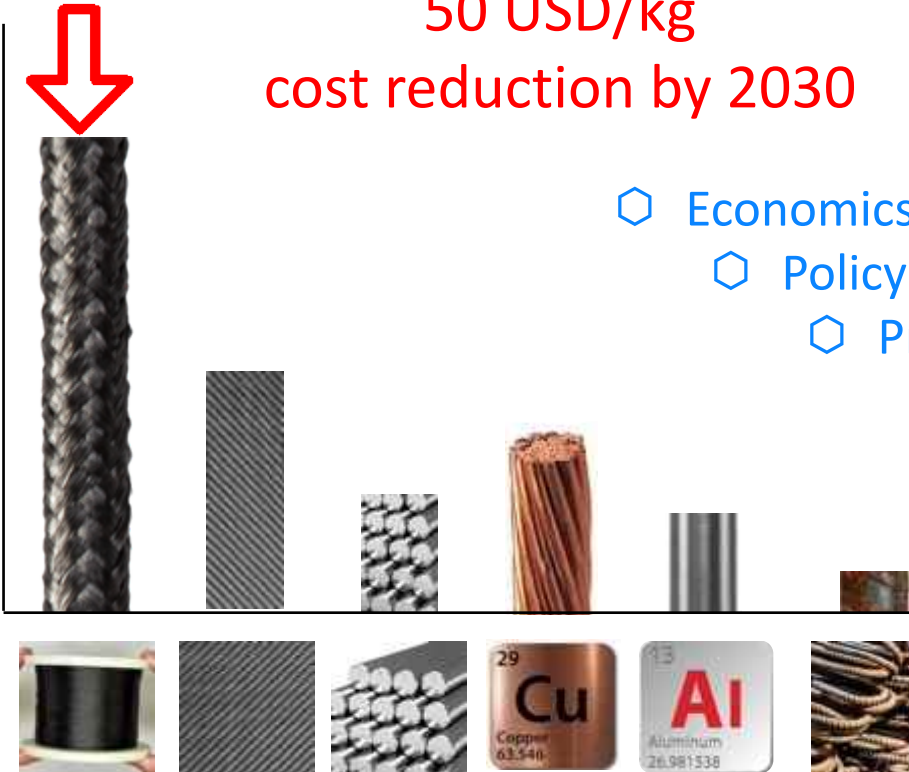
- Carbon Materials must achieve cost parity with incumbents
- Total cost of ownership/LCA at product level
- Embodied energy, CO₂

SunShot Goal



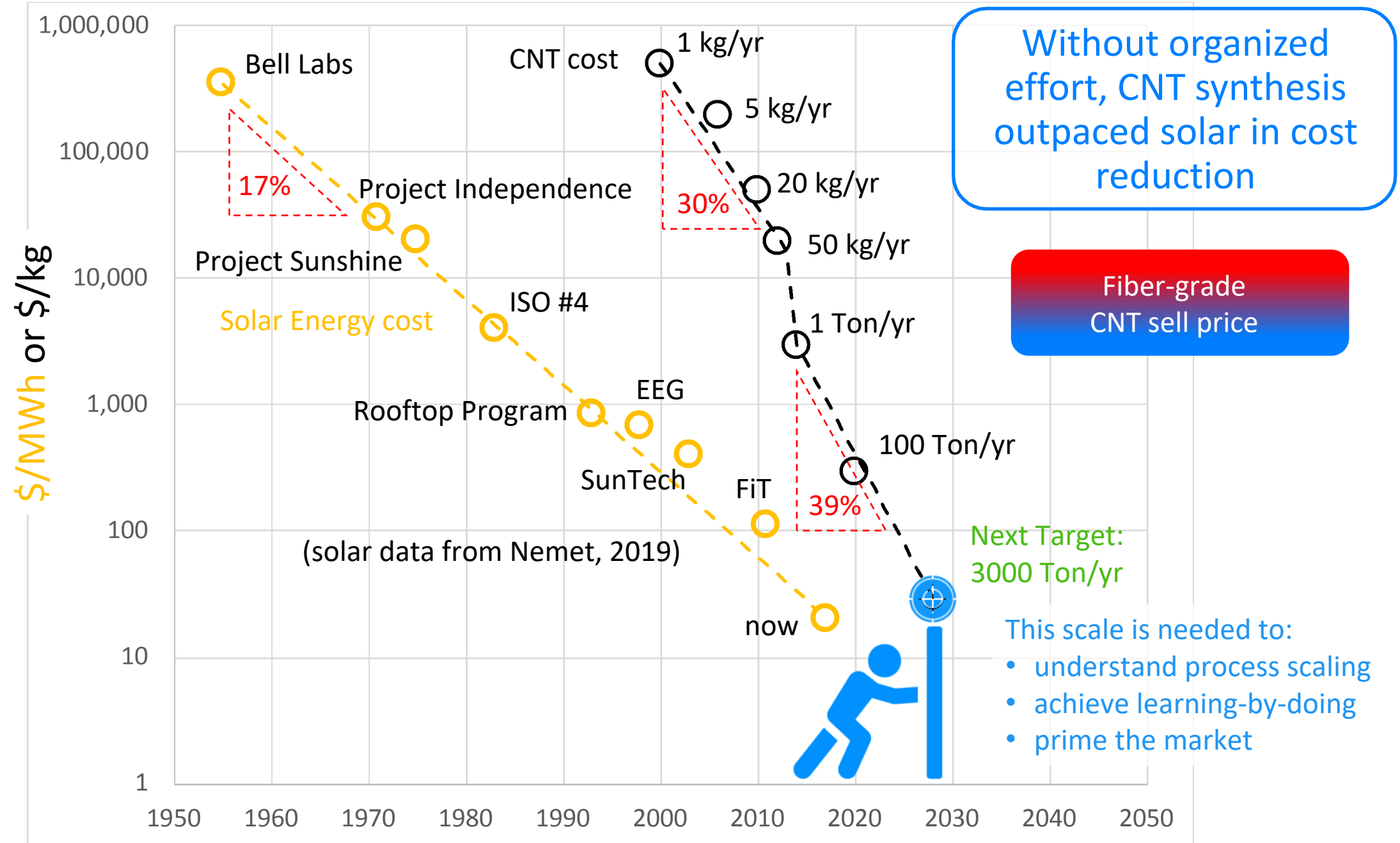
CarbonShot Goal

Price / energy / CO₂ / function



- Economics
- Policy
- Product design

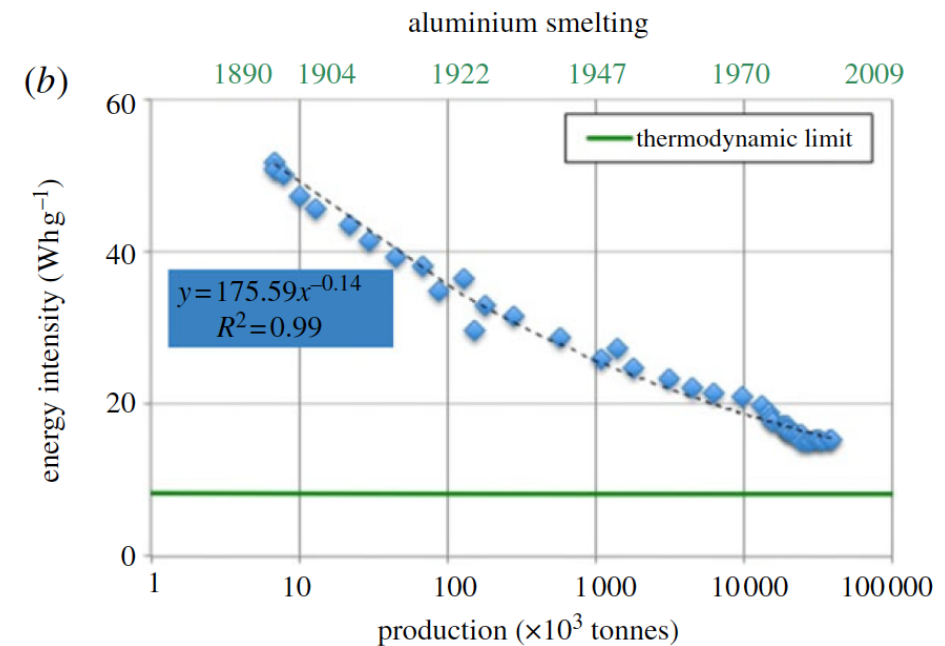
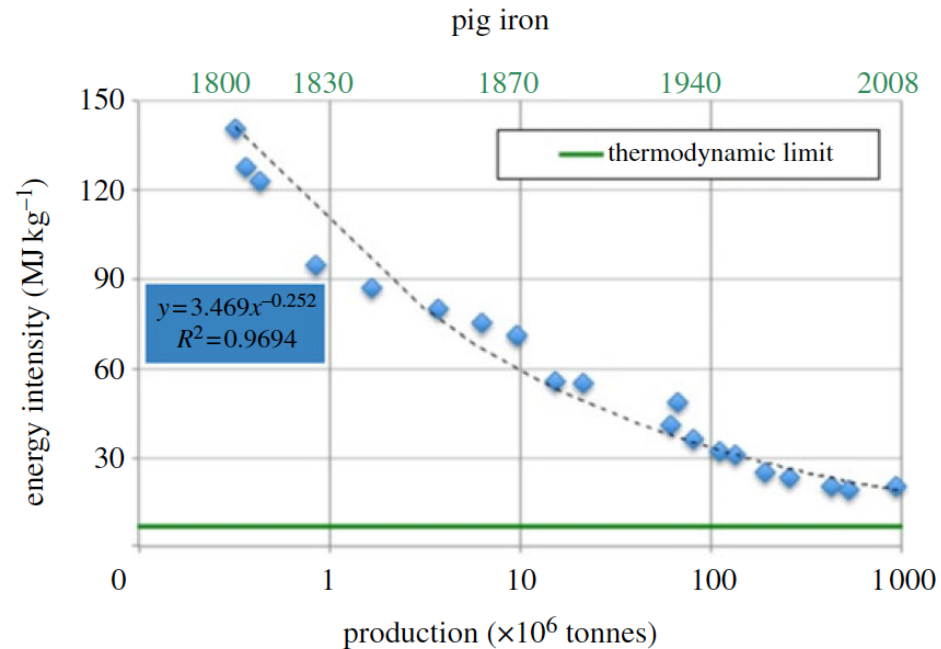
COST AND COST REDUCTION: COMPARISON TO SOLAR



HISTORICAL EXAMPLES OF MATERIAL COST REDUCTION

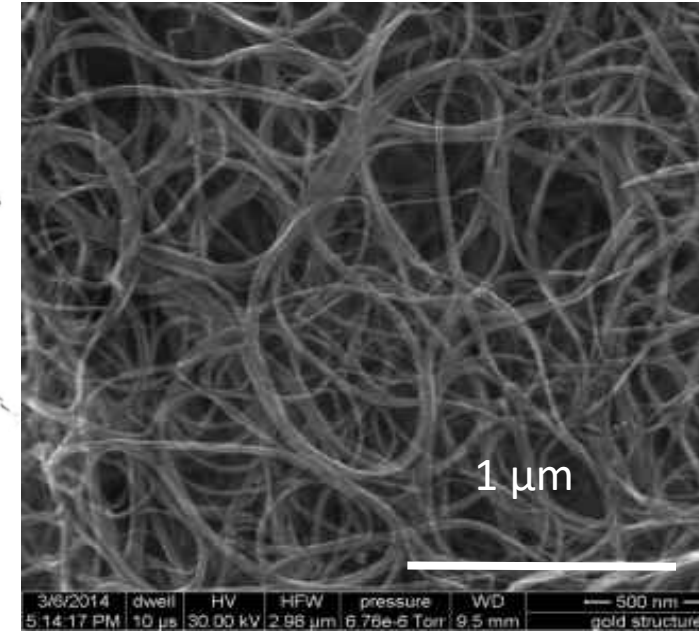
- Steel and aluminum are great examples
- Both were known for decades/centuries before mass scaling
- Considered specialty (even used for jewelry)
- Introduced as top-performing materials
- Gradually became commodities
- Material energy intensity drops with production scale
- By itself, elapsed time is not important
- Cost follows energy intensity
- Fast development and introduction of products is critical

Can we use science
to lower cost faster?

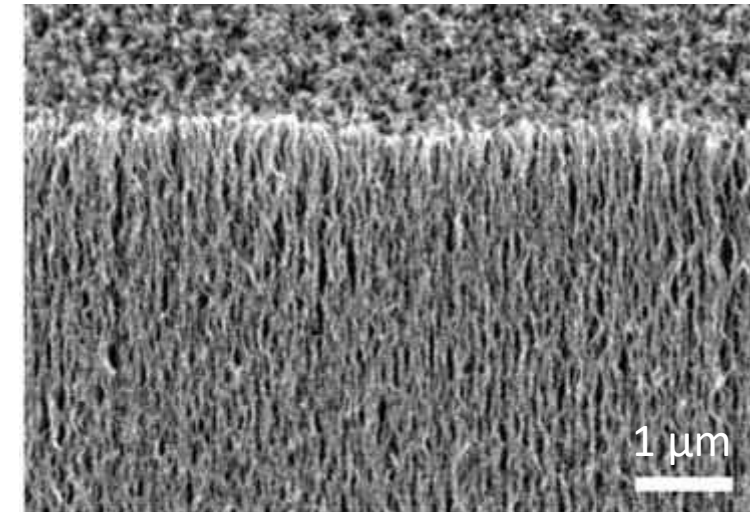


HOW ARE CNTs MADE?

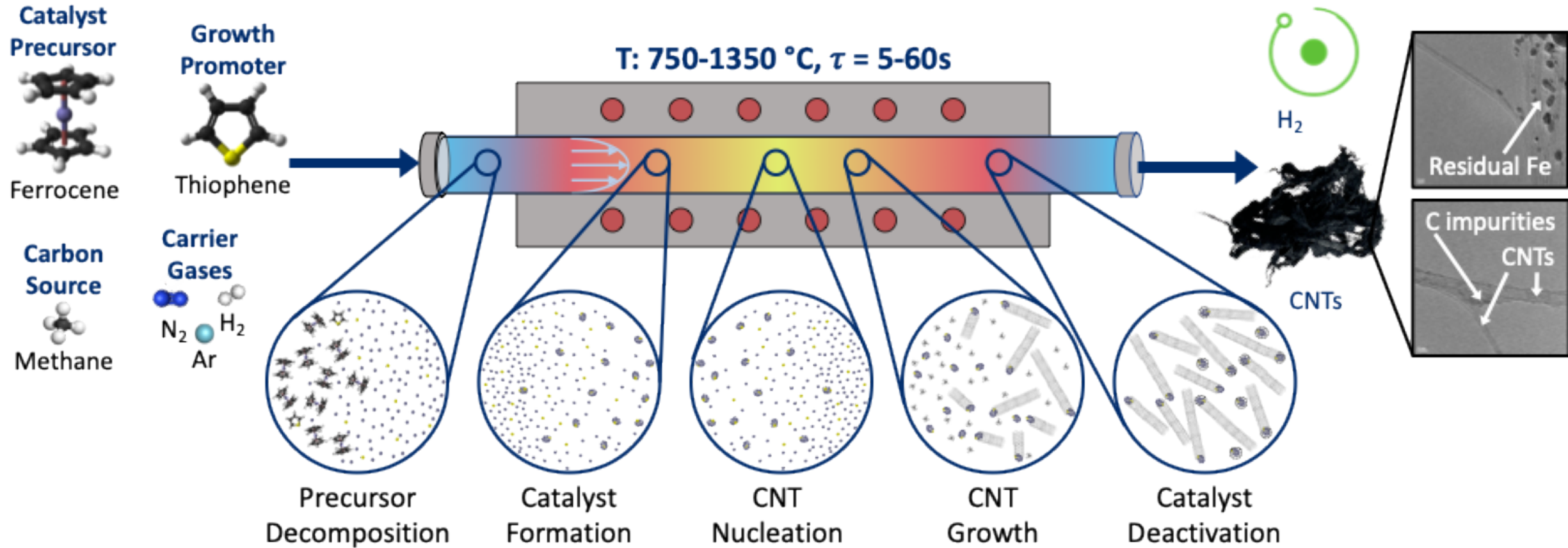
- Carbon source (graphite, CO, hydrocarbons)
- Metal catalyst (1-5 nm particles)
- Dilution (hydrogen, nitrogen)
- Moderate temperature (750-1300 C)
- Various reactor configurations
 - Fixed/floating bed, unsupported catalyst (no support), surface-supported
- Up to ~2015, no attention to efficiency
- Up to ~2020, low reactor understanding
- 2018-2018
 - Rice, Shell, and ARPA-E launch a focused program on understanding CNT reactors
 - Other participants (Huntsman, Stanford, U Cambridge, Politecnico di Milano...)
 - Reactor data, process/plant modeling
 - Fully-integrated program (methane to fibers)



Hata et al, Science 2004



CNT SYNTHESIS VIA CONTINUOUS FLOW REACTORS



⬡ Largely treated as “black boxes” so far

⬡ Reactor/reaction efficiency

⬡ Catalyst utilization

⬡ Selectivity to CNTs

CNT SYNTHESIS: NEW LEARNING CURVE



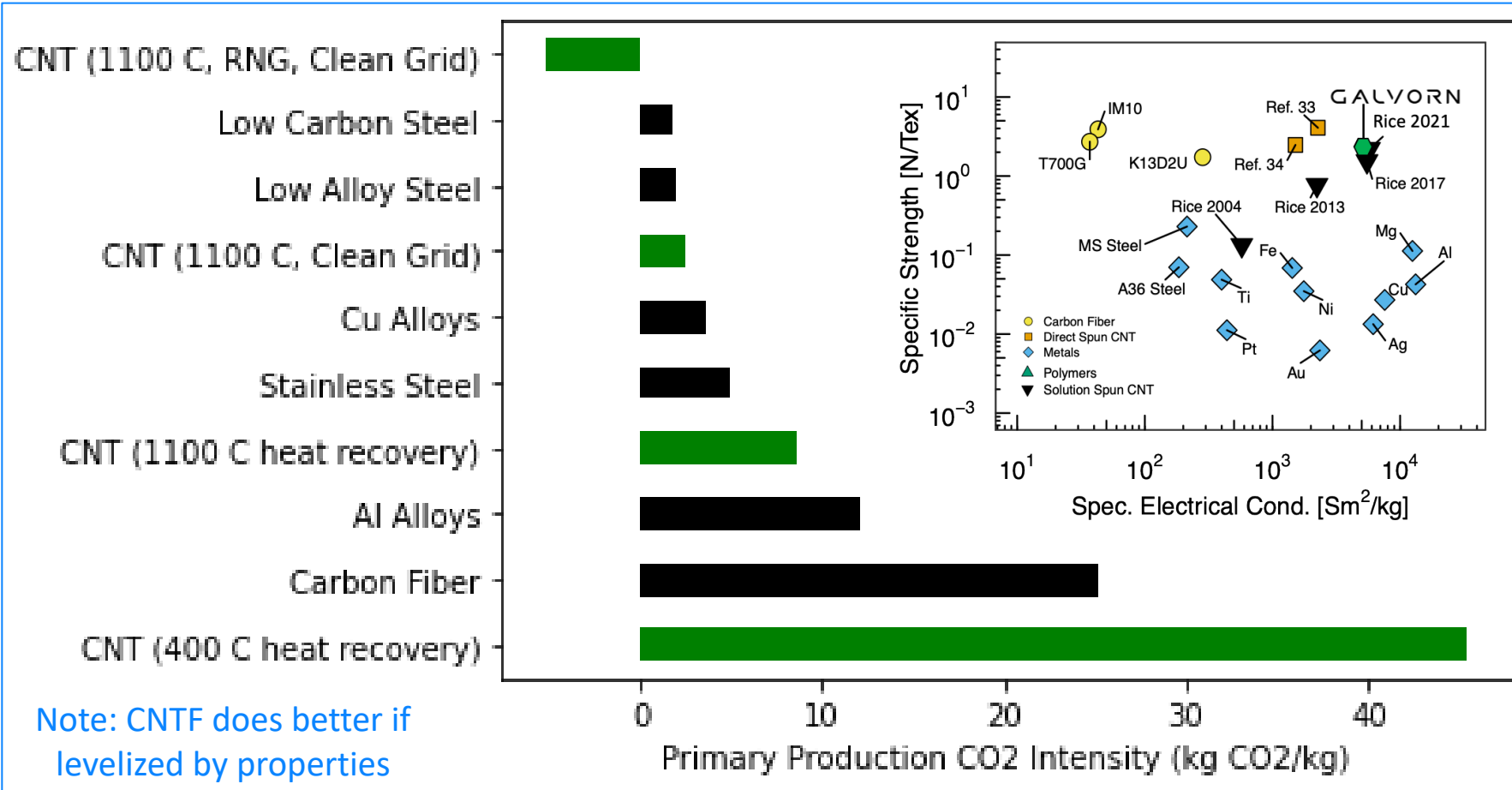
- ⬡ CNTs grown from methane
- ⬡ Conversion from 0.05% (2019) to ~30% (now)
- ⬡ Selectivity from ~70% to > 90%
- ⬡ Continuous production, inexpensive catalyst & dilution gases
- ⬡ Hydrogen co-production proven
- ⬡ Embodied energy below 200 MJ/kg
 - ⬡ Better than carbon fibers, aluminum
 - ⬡ Could drop another 10x with further intensification



Carbon nanotubes at reactor exit

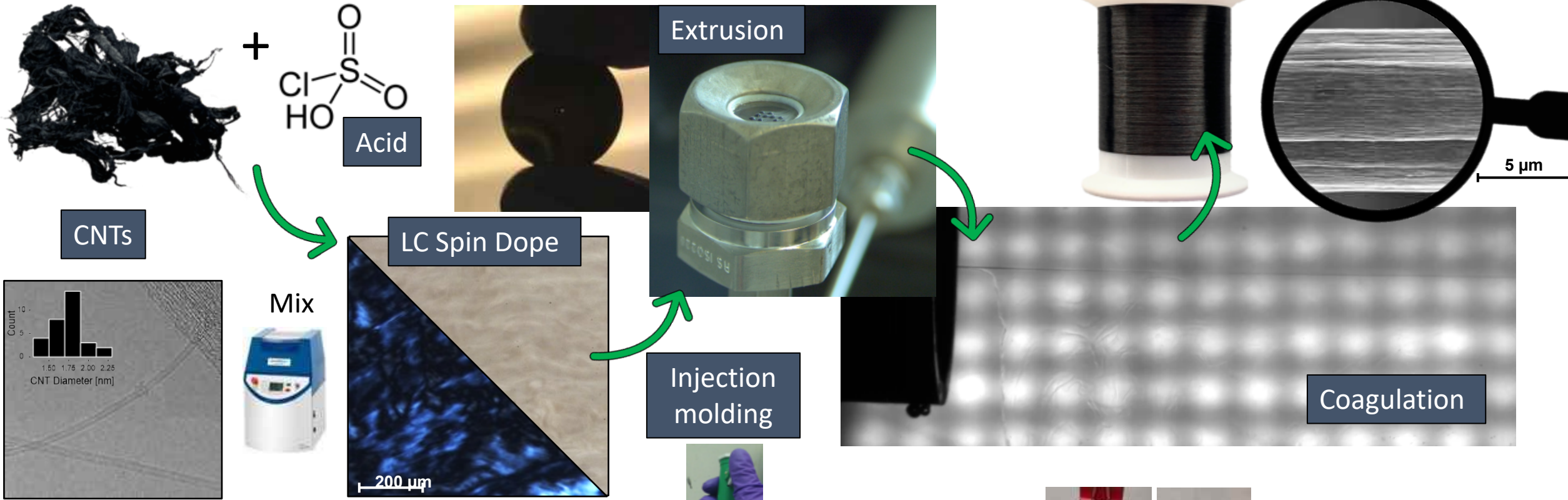
- ⬡ Proven at ~5 kg/yr
- ⬡ ~1,000x cost reduction
 - ⬡ Ready for demo-scale
- ⬡ Product considerations:
 - ⬡ High-quality maintained
 - ⬡ Fiber-grade CNTs
 - ⬡ High strength
 - ⬡ High electrical cond.
 - ⬡ High thermal cond.

CARBON-NEGATIVE MATERIALS!



- ⬡ On US grid and with heat integration, CNTs are competitive with Carbon Fibers & Aluminum
- ⬡ On clean grid, they are cleaner than industrial metals
- ⬡ When using renewable natural gas, they are carbon negative!

FROM CNT POWDER TO MACRO MATERIALS



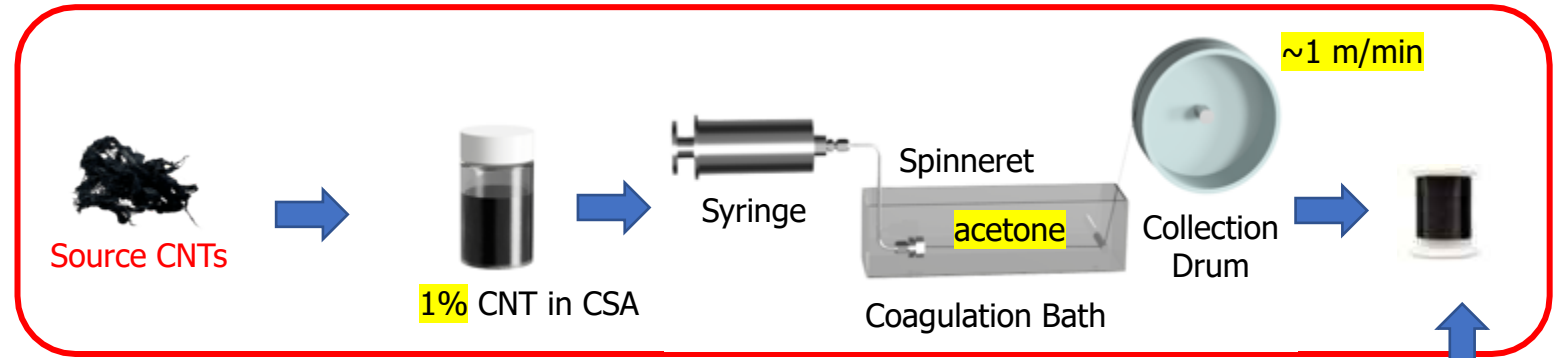
- Use liquid crystal (LC) ordering and flow to create order
- Lock in order and densify with coagulant
- Solution processing extends to other geometries



FIBER SPINNING PROCESS INTENSIFICATION

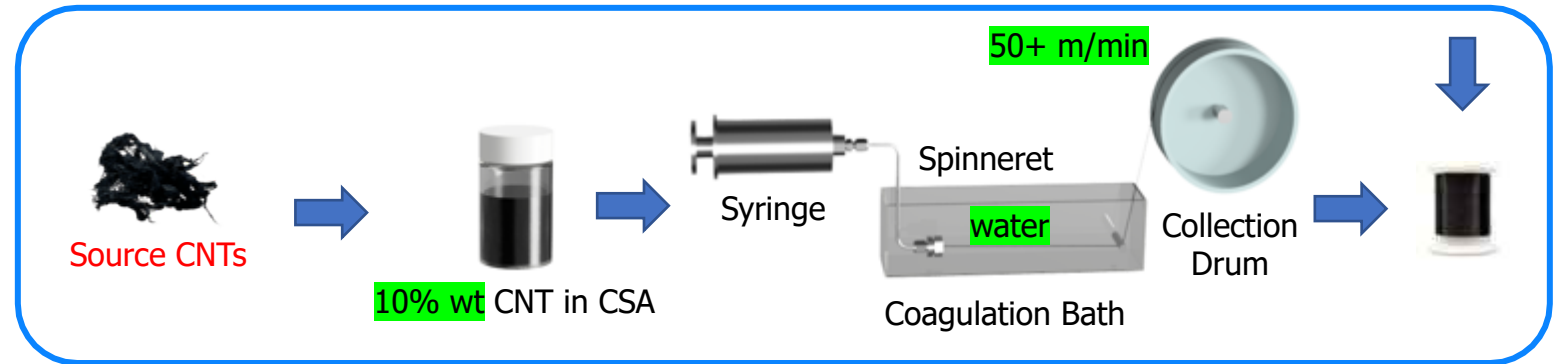
Conventional spinning

- ⬡ Slow (~1 m/min)
- ⬡ Low CNT concentration
 - ⬡ 0.5% to 2%
- ⬡ Uses organics (acetone)
 - ⬡ Cost
 - ⬡ CO₂ footprint
- ⬡ End-of-life questions



GS-spinning

- ⬡ Fast (30+ m/min)
- ⬡ High CNT concentration
 - ⬡ 10%, maybe higher
- ⬡ No organics
- ⬡ Full recyclability demonstrated



same properties ✓

- ⬡ Over 500x reduction in variable costs
- ⬡ Production much simpler than current carbon fibers
- ⬡ Fits existing industrial platform for scale-up

CNT FIBERS vs PAN-BASED CARBON FIBERS

Chemical Reactions

Splitting of the hydrocarbon, purification*, catalyst removal.

*Purification may not be necessary if reaction is optimized.

3

Comparative
Process Complexity

10

Chemical Reactions

Cracking of naphtha or propane, steam methane reforming, Haber-Bosch process, ammoxidation, PAN polymerization, pre-treatment, oxidation, 2x carbonization, and surface treatments.

2

CNT
Fiber

PAN-
based
Carbon
Fiber

4

Phase Changes

Separation of propane or naphtha from natural gas or oil, dissolution of PAN in DMSO, DMF, or DMAc, coagulation in methanol, and washes.

2

Mechanical Processes

Fiber spinning and winding.

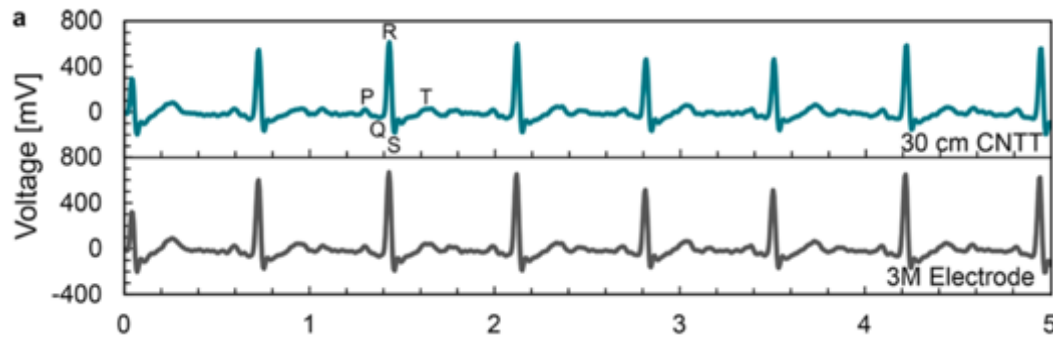
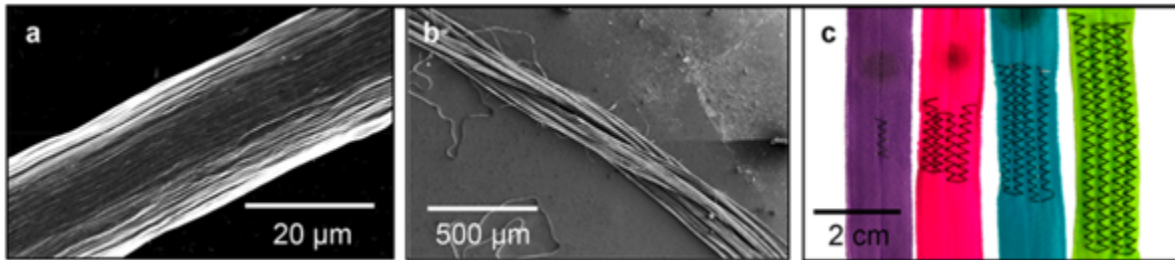
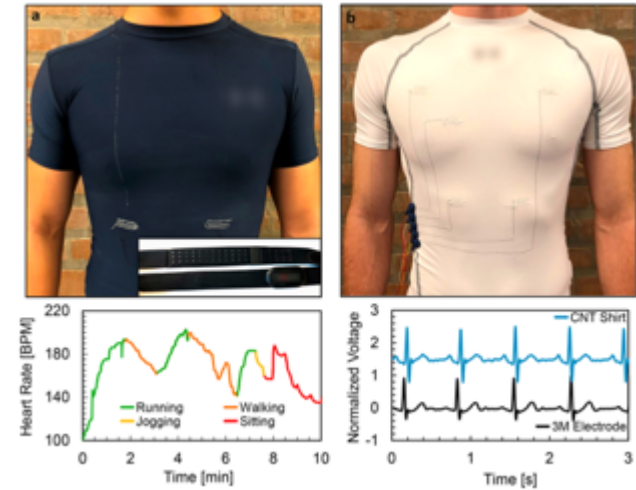
4

Mechanical Processes

Fiber spinning, 2x winding, and sizing.

APPLICATIONS OF STRONG, FLEXIBLE CNT CONDUCTORS

- Combination of softness and mechanical/electrical properties is great for wearable applications
- Comfortable, reusable sensors for the wrist
- Sewn in sensors for heart-rate-monitoring T-shirt



DESIGN CHANGES AT DEVICE ARCHITECTURE LEVEL



Ponte di Tiberio (Rimini, Italy)

ARCH BRIDGE: COMPRESSION

$$\text{Material property} = \frac{\text{compressive strength}}{\text{density}}$$

$$\text{Istrian stone} = \frac{171 \text{ MPa}}{2690 \text{ kg/m}^3} \approx 60,000 \text{ m}^2/\text{s}^2$$

$$\text{Steel} = \frac{152 \text{ MPa}}{7850 \text{ kg/m}^3} \approx 20,000 \text{ m}^2/\text{s}^2$$



Golden Gate Bridge (San Francisco)

SUSPENSION BRIDGE: TENSION

$$\text{Material property} = \frac{\text{tensile strength}}{\text{density}}$$

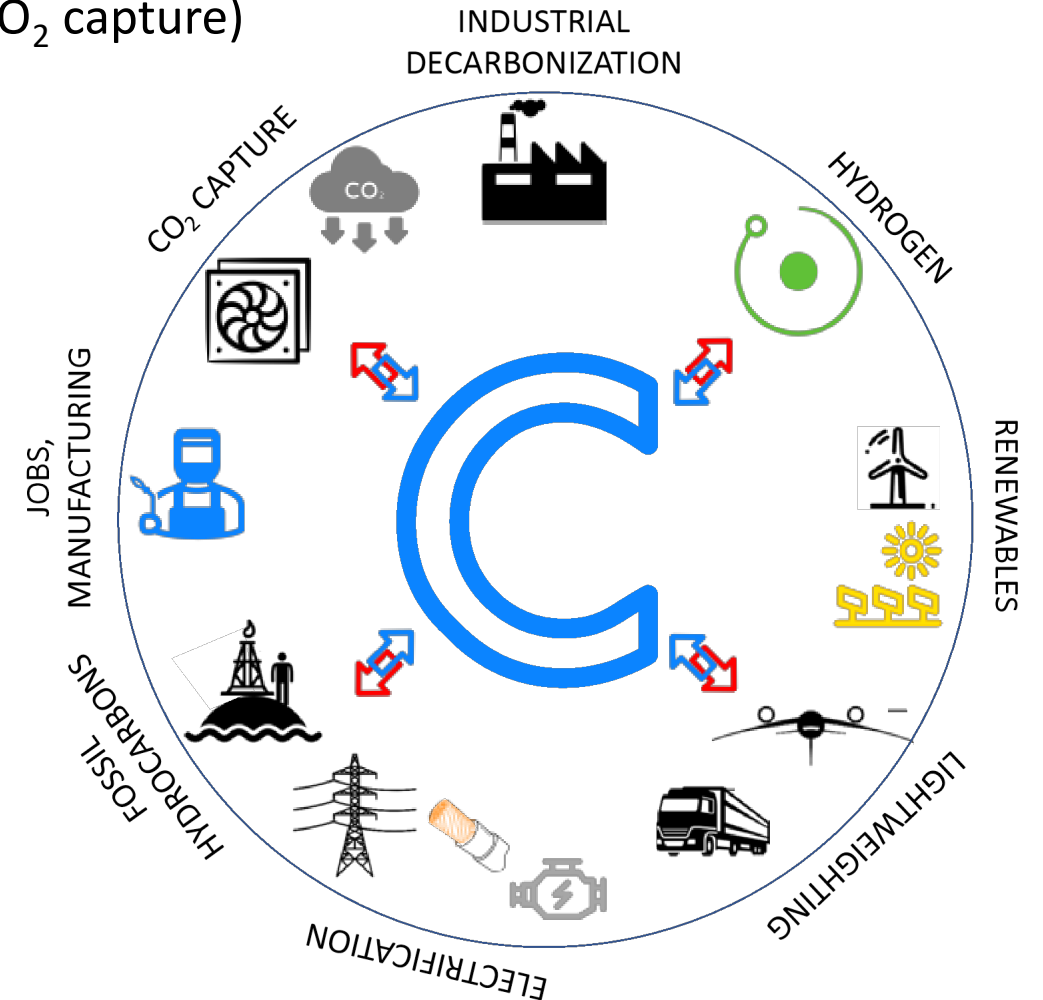
$$\text{Istrian stone} = \frac{16.7 \text{ MPa}}{2690 \text{ kg/m}^3} \approx 6,200 \text{ m}^2/\text{s}^2$$

$$\text{Steel} = \frac{550 \text{ MPa}}{7850 \text{ kg/m}^3} \approx 70,000 \text{ m}^2/\text{s}^2$$

- ⬡ New **properties** can enable **architectural redesign**
- ⬡ Building a **new industry** will require **coordination**

CLIMATE AND ECONOMIC IMPACT AT SCALE

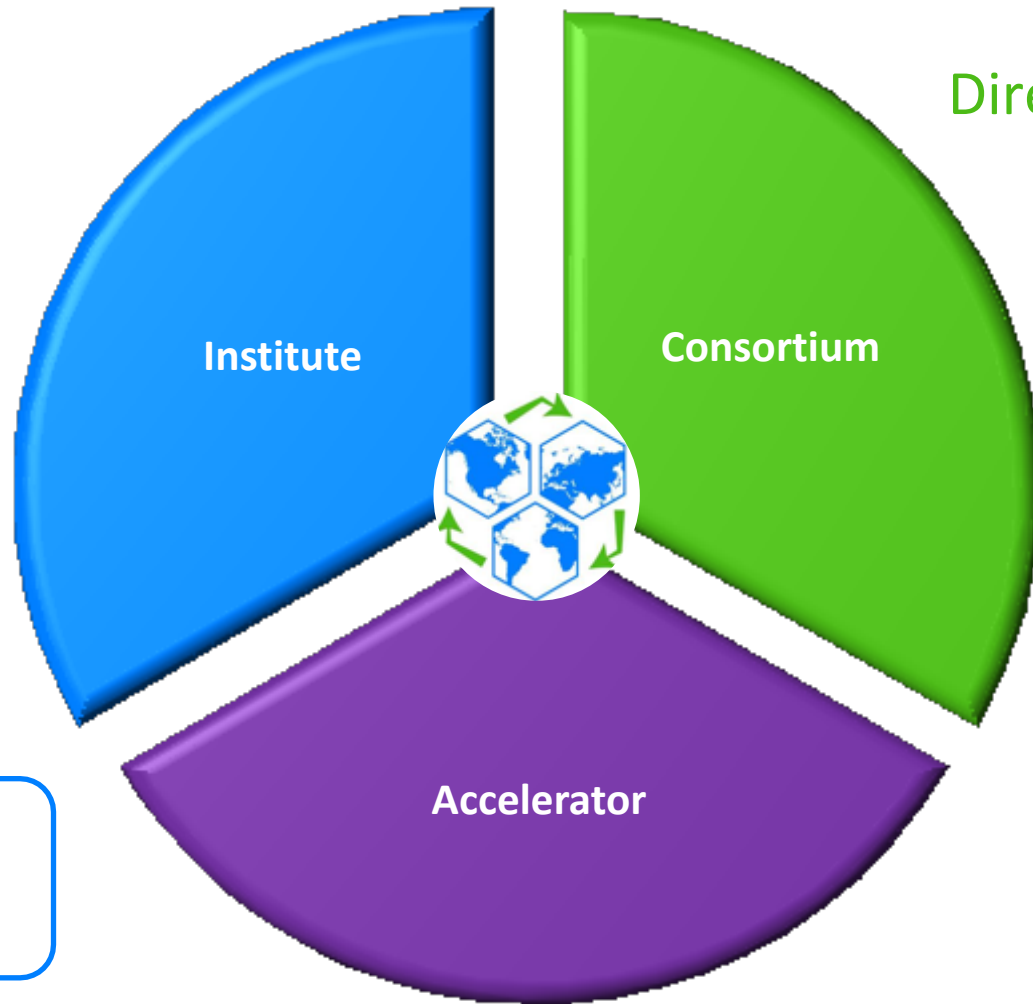
- ⬡ Material can be CO₂ negative if made from renewable natural gas (-4 kg CO₂/kg CNTF)
- ⬡ Eliminate energy costs of mining and producing industrial metals (~12% of world energy use)
- ⬡ Eliminate CO₂ emissions from mining and producing industrial metals (~3 GT CO₂/yr)
- ⬡ Fix and utilize 1+ GT/yr of solid carbon (equivalent to 3.7 GT CO₂ capture)
- ⬡ Co-produce 300+ MT/yr of Hydrogen
- ⬡ Preserve fossil hydrocarbon value chains
- ⬡ Promote fledging renewable hydrocarbon production
- ⬡ Additional impact in
 - ⬡ Lightweighting
 - ⬡ Electrification
 - ⬡ Material circularity
 - ⬡ 2-nd generation renewables
- ⬡ Over 2 T/yr USD Industry
- ⬡ Secure supply chains
- ⬡ US manufacturing
- ⬡ US jobs



Accelerate the emergence of an industry and large markets based on value-added carbon



Dr. Marie Contou-Carrere
Executive Director
mncontou@rice.edu



Direct and fund research in high impact areas

- Engage corporations
- Engage startups
- Organize the innovation ecosystem
- Engage with federal government
 - Agencies
 - National labs
- Engage strategically with other leading climate academic centers

Foster & accelerate the creation of companies in key technology areas

OPEN COLLABORATION MODEL

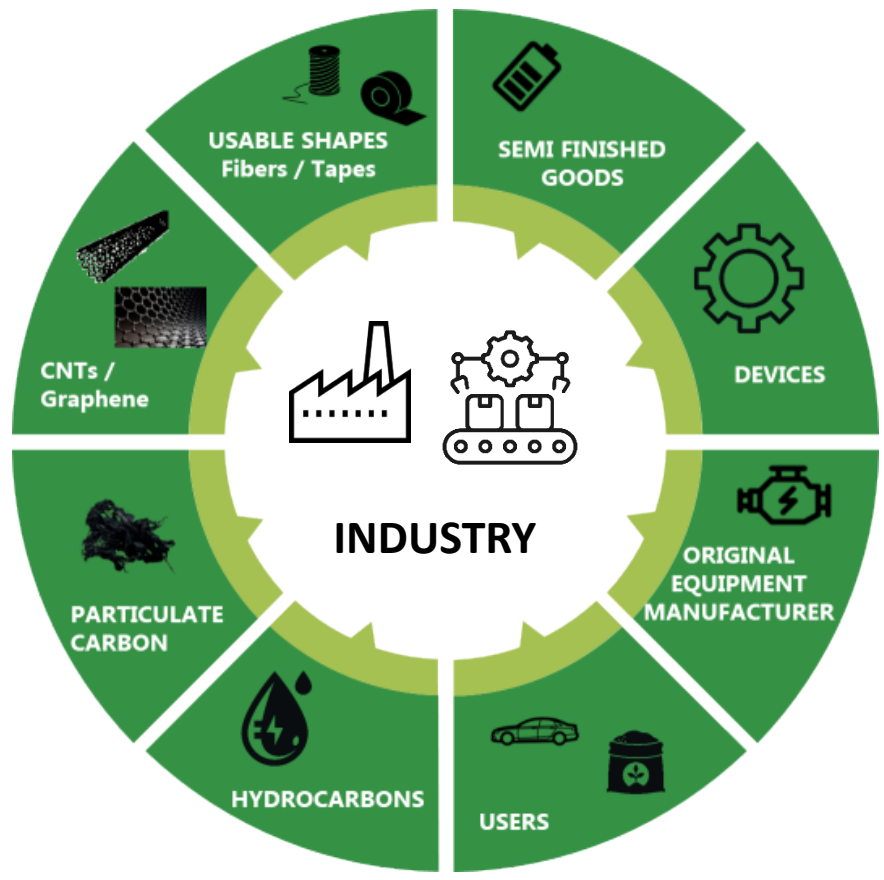


Academia & Federal Labs

Interfacing / Integrating with Industrial R&D

Launched in December 2019

100+ researchers
20+ research organizations



CURRENT PROJECT MAP

~\$3 MM so far
~\$2 MM in contracting



Maboudian



Parikh



McFarland



Maruyama



Kladitis



Goulthrope



Stach



Pasquali



Ajayan



Masiello



Biswal



Wehmeyer



Naik



Castellon

International collaborators



Boies



Vilatela



Carfagni



Maestri



Kim



CREATING THE FUTURE



Informed by industry needs

Neutral ground for corporate partners

Academically grounded by Rice University

Independently steered by centralized governance

**Mark Goulthorpe, MIT
House in 6 parts, WOJR**



CURRENT GROUP

Steven Williams, CHBE
Tulane



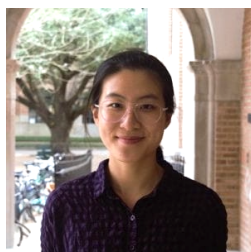
Oliver Dewey, CHBE
CO School of Mines



Mitchell Trafford, CHBE
U Tulsa



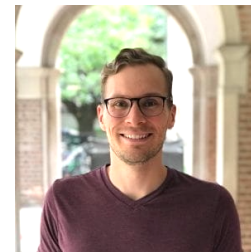
Muxiao Li, CHEM
U Maryland



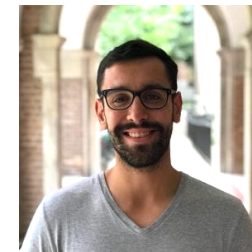
Anavi Benavides, CHEM
TEC de Monterrey



Cedric Ginestra, CHBE
UT Austin



Ivan Siqueira, CHBE
PUC Rio



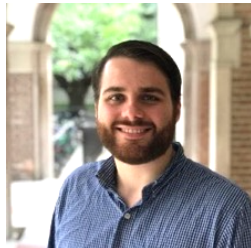
Michelle Duran, CHEM
U de Costa Rica



Alex Dantzler, CHBE
UT Austin



Arthur Sloan, CHBE
Auburn U



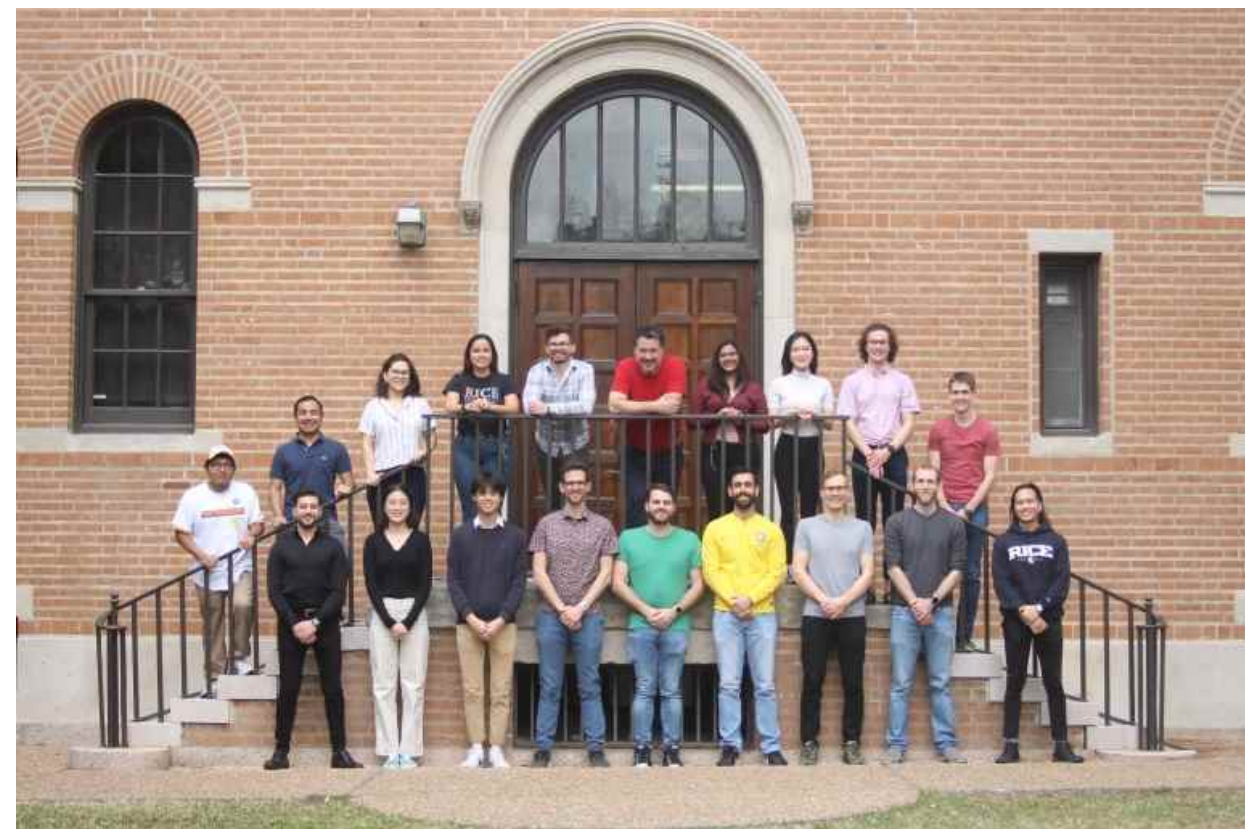
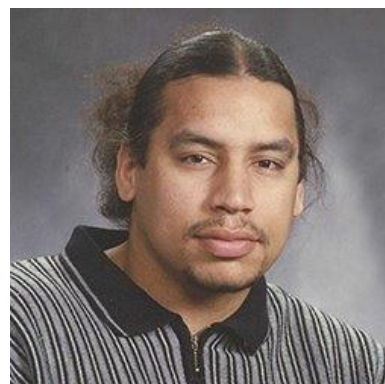
Lily Gong, CHBE
Auburn U



Jui Junnakar, CHBE
BITS Pilani



Joe Khoury, CHBE
Cleveland State U



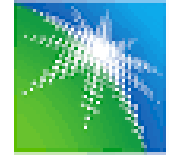
Close collaboration with Dr. Glen Irvin



FUNDING & COLLABORATIONS



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saudi aramco



Prysmian
Group



arpa.e
CHANGING WHAT'S POSSIBLE

سابك
sabik



BSF
United States - Israel
Binational Science Foundation

HUNTSMAN
Enriching lives through innovation



ExxonMobil

TECHNION
Israel Institute of Technology



POLITECNICO
DI MILANO

KIST
Korea Institute of
Science and Technology

Mitsubishi Corporation
(Americas)



Carbon Hub

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